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PHYSICAL REVIEW

A CORPUSCULAR QUANTUM THEORY OF THE SCATTERING OF POLARIZED X-RAYS

By G. E. M. Jauncey

Abstract

The methods of a previous paper, which gave a corpuscular quantum theory of the scattering of unpolarized x-rays are here applied to the scattering of polarized x-rays. A formula is derived for the intensity scattered in any direction, and from this an expression is obtained for the ratio of the intensity scattered in the direction of the electric vector to that scattered in a direction perpendicular both to the electric vector and to the primary beam. The intensity scattered in the direction of the electric vector is not zero as it should be on the classical theory. Taking the polarizing angle as the angle of scattering which gives completely polarized rays from unpolarized primary rays, a formula is derived which shows that for very long wave-lengths the polarizing angle is 90°, but for short wave-lengths it is less than 90°.

1. Introduction

In a previous paper,[1] the writer has applied a corpuscular quantum theory to the scattering of unpolarized x-rays. In the present paper the method of the previous paper is applied to the problem of the scattering of polarized x-rays. Polarization of x-rays has up to the present time been measured experimentally by scattering the primary beam by some substance of low atomic weight. The intensity of the rays scattered in a plane at right angles to the primary rays is measured in various directions. If the intensity in this plane becomes zero in a certain direction and is a maximum in a direction at right angles to the first direction, the primary x-rays are said to be plane polarized. The question however arises as to the efficiency of this method of determining polarization. In other words, how efficient is the scattering substance as an analyser. On the classical theory due to Thomson,[2] a minimum intensity other than zero would mean incomplete polarization. Does the corpuscu-

[1] G. E. M. Jauncey, Phys. Rev. **22**, 233 (1923)

[2] J. J. Thomson, Conduction of Electricity through Gases, 2nd. Ed. p. 325

lar quantum theory of the previous paper require a minimum intensity of zero in order to establish complete polarization of the primary x-rays? It is the purpose of this paper to answer this question.

2. Scattering of Long Wave-length X-Rays

As in the previous paper it will be assumed that scattering is according to the Thomson theory when long wave-length x-rays are scattered by electrons. In this case the corpuscular theory supposes that the electron has negligible energy imparted to it by the x-ray corpuscle. Referring to Fig. 1 and applying the argument of the previous paper, the x-ray

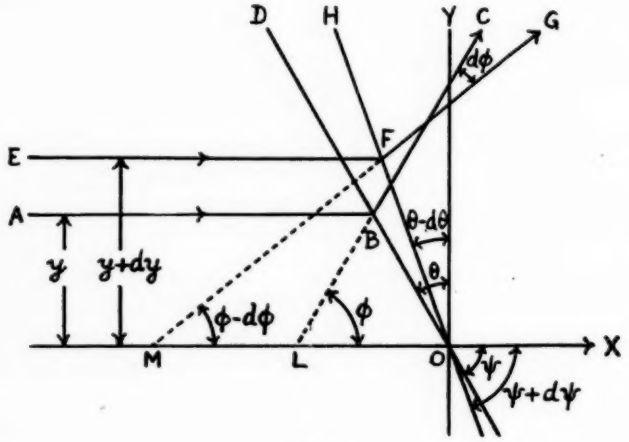

Fig. 1

corpuscle approaches the electron whose center is at O on the axis of x. If the line of flight of the corpuscle is at a distance y from the axis of x, the corpuscle is scattered in the direction ϕ. The problem is to discover the relation between y and ϕ. In the previous paper the scattering was taken as symmetrical about the axis of x; but now the effect of polarization must be considered.

As before, we have Eq. (1), provided that the line of flight of the scattered corpuscle lies in the same plane as the center of the electron and the line of flight of the corpuscle before scattering. Hence

$$n_\phi = -\frac{n_0 y}{R^2 \sin\phi} \frac{dy}{d\phi}, \tag{1}$$

where n_0 is the number of corpuscles crossing unit area placed perpendicular to the primary beam in unit time, and n_ϕ is the number of corpuscles scattered by the electron in a direction ϕ and crossing unit area in unit

time at a great distance R from the electron. Porceeding from this as in the previous paper, we have the intensity relation

$$I_\phi = -\frac{I_0 y}{R^2 \sin\phi} \frac{dy}{d\phi}, \tag{2}$$

where I_ϕ is the intensity scattered by one electron in the direction ϕ and I_0 is the intensity of the primary rays. Let the primary x-rays be polarized so that the electric vector makes an angle χ with the plane of Fig. 1. The scattered intensity in the direction ϕ of the figure is then given by Thomson's theory as

$$I_\phi = (I_0 e^4/R^2 m^2 c^4)\ (1-\cos^2\chi \sin^2\phi), \tag{3}$$

where e, m and c have their usual significance. Equating the two expressions for I_ϕ, Eqs. (2) and (3), and integrating, we have

$$y^2 = (2e^4/3m^2c^4)\ \{3\sin^2\chi(1+\cos\phi)+\cos^2\chi(1+\cos^3\phi)\}, \tag{4}$$

since $y=0$ when $\phi=\pi$. The greatest value of y occurs when $\phi=0$ and $\chi=\pi/2$. This is the semi-major axis of the electron plus that of the corpuscle. Let this length be called a and we have

$$a = 2e^2/mc^2 = 5.63\times10^{-13}\ \text{cm}. \tag{5}$$

Eq. (4) may therefore be written

$$y^2 = (a^2/6)\ \{3\sin^2\chi(1+\cos\phi)+\cos^2\chi(1+\cos^3\phi)\}, \tag{6}$$

Referring to Fig. 1, $y = OB\cos\theta = r\cos\phi/2$, where $r = OB$. Substituting r for y in Eq. (6) we obtain

$$r^2 = (a^2/3)\ \{3\sin^2\chi+\cos^2\chi(1-\cos 2\theta+\cos^2 2\theta)\} \tag{7}$$

This is the spherical polar equation of the locus of the center of the x-ray corpuscle at the instant when scattering takes place, the center of the electron being supposed to remain fixed in space. The radius vector r is the sum of the semi-diameter of the electron and that of the x-ray corpuscle in the direction (θ, χ). According to this theory, then, the phenomenom of polarization is associated with an asymmetry of r, and since there is no reason why the electron should be oriented with respect to the direction of the rays, it seems more probable to assume this polarization to be due to asymmetry of the x-ray corpuscle.

The section of the surface (7) by the cone $\theta=0$ is

$$r^2 = (a^2/3)\ (1+2\sin^2\chi). \tag{8}$$

If y is less than this value of r then the x-ray corpuscle is scattered. The area of curve (8) is $2\pi a^2/3$. The total scattering by the electron is therefore in virtue of Eq. (5)

$$(8\pi e^4 I_0)/(3m^2c^4). \tag{9}$$

This is, as it should be, the same as the total energy scattered according to Thomson's theory.

3. Scattering of Short Wave-length X-Rays

Proceeding as in the previous paper, and referring to Fig. 1, it is assumed that when the impinging corpuscle arrives at B there is a sudden interaction between the corpuscle and the electron, the corpuscle being deflected so as to travel in the direction ϕ. It might be supposed that the angle BOY or θ of Fig. 1 remains unchanged for a given value of y/a irrespective of the momentum h/λ of the impinging corpuscle. However, in order to make the case more general, let us suppose that "distortion" takes place as described in the discussion of the previous paper. There it was supposed that the angle BOY had the value A for large values of h/λ, where

$$\tan A = \frac{\sqrt{1+F}}{1+\alpha} \tan \theta = \sqrt{1+F} \cdot \tan \phi/2. \tag{10}$$

In Eq. (10) F is a function of $\alpha = h/mc\lambda_0$ which becomes zero when $\alpha = 0$. λ_0 is the wave-length of the primary x-rays. We now replace ϕ of Eq. (6) by $2A$ and obtain

$$y^2 = (a^2/6)\ \{3\sin^2\chi(1+\cos 2A)+\cos^2\chi(1+\cos^3 2A)\}. \tag{11}$$

Eq. (11) holds for all values of h/λ_0, whereas Eq. (6) only holds when $h/\lambda_0 = 0$. Applying Compton's change of wave-length formula[3] and Eqs. (1), (10) and (11), and supposing that the value of I_ϕ in the forward direction, $\phi = 0$, is the same as that on Thomson's theory for the same direction, we have, following the method of the previous article,

$$I_\phi = K\frac{\sin^2\chi+\cos^2\chi\cos^2\phi-2F\cos 2\chi\sin^2\phi/2+(4F\cos^2\chi+F^2)\sin^4\phi/2}{(1+F\sin^2\phi/2)^4\,(1+2\alpha\sin^2\phi/2)}, \tag{12}$$

where $K = I_0e^4/R^2m^2c^4$.

For scattering in the plane at right angles to the direction of the primary x-rays, we have, putting $\phi = \pi/2$,

$$I_{\pi/2} = \frac{I_0e^4}{R^2m^2c^4} \cdot \frac{\sin^2\chi - F\cos 2\chi + F\cos^2\chi + F^2/4}{(1+F/2)^4\,(1+\alpha)}. \tag{13}$$

Putting $\chi = 0$ in Eq. (13) we have the intensity I' in the direction of the electric vector, while putting $\chi = \pi/2$ we have the intensity I'' scattered in a direction perpendicular to the electric vector. The ratio I'/I'' is not zero as it should be on the classical theory but is

$$k = I'/I'' = F^2/4(1+F/2)^2. \tag{14}$$

In the previous paper F was given two values, namely 2α and $2\alpha+\alpha^2$, and we therefore obtain

$$I'/I'' = \frac{\alpha^2}{(1+\alpha)^2} \quad \text{or} \quad \frac{\alpha^2+\alpha^3+\alpha^4/4}{(1+\alpha+\alpha^2/2)^2}. \tag{15}$$

[3] A. H. Compton, Phys. Rev. **21**, 483 (1923)

These two values of I'/I'' are very nearly equal for small values of α. In fact for ordinary x-rays, where the wave-length is usually greater than 0.24 A, the value of α is less than 0.1 and the ratio is approximately α^2 or less than 1 per cent. On the other hand for gamma rays where α is of the order unity the value of the ratio is about 30 per cent. It is perhaps worth noticing that if I_ϕ of Eq. (12) is averaged for all values of χ between 0 and 2π the expression for I_ϕ of the previous paper, Eq. 21, is obtained. This is the expression for I_ϕ when unpolarized x-rays are scattered.

From Eq. (13) it is obvious that I_ϕ never becomes zero in the cone $\phi=\pi/2$ unless F is zero. If we put $\chi=0$ in Eq. (12) we find that I_ϕ becomes zero for $\phi=\phi_p$ where

$$\cos\phi_p = F/(2+F). \tag{16}$$

ϕ_p may be called the polarizing angle because when unpolarized x-rays are scattered in this direction the scattered rays are completely polarized. The polarizing angle for long wave-length x-rays ($\alpha=0.0$) is 90° but that for x-rays of wave-length, say, 0.12 A ($\alpha=0.2$) is about 80°.

Eqs. (15) and (16) are each susceptible of experimental verification. Compton and Hagenow,[4] using the scattering method, have studied the polarization of x-rays which had been polarized by scattering unpolarized x-rays at right angles. However the wave-lengths which they used were too long and the experimental error was too great for a test of Eq. (15). For this reason experiments are now in progress in this laboratory to test the correctness of Eqs. (15) and (16), using short wave-length x-rays.

WASHINGTON UNIVERSITY,
ST. LOUIS, MO.,
October 15, 1923.

[4] Compton and Hagenow, Phys. Rev. **18**, 97 (1921)

A PERIODIC LAW OF ATOMIC RADII

By Wheeler P. Davey

Abstract

Packing radii of elements; periodic relationship is evident if the radii of the 44 elements for which the values have been determined from x-ray crystallographic data, are plotted as a function of the number of electrons in the outer shell. Beginning with each rare gas, the curves are similar, the ratios of the ordinates being constant for the following 9 or 10 elements, as far as the values are known. By making use of the new law, rough predictions are made of the radii of ten other elements whose crystal structures have not yet been experimentally determined.

MOST of the chemical properties and many of the physical properties of the chemical elements show periodic relationships when the elements are arranged in the order of their atomic numbers. The relationship between these properties and the architecture of the atoms is brought out in a modification of the Mendelejeff table proposed by Langmuir.[1] It is the purpose of this paper to point out one more such periodic law.

The effective radius (packing radius) of the atom of an element may be at once determined from the distance of closest approach of atoms in the crystal of the element. These distances have been tabulated by A. W. Hull[2] for the various elements whose crystal structures were known at that time. Additional measurements are available for the atoms of the inert gases (except He),[3] beryllium,[4,5] potassium,[6] vanadium,[7] germa-

[1] Langmuir, Jour. Am. Chem. Soc. **91,** 868 (1919). Such a table may be put in more convenient form by making the following changes in the ordinary Mendelejeff table. Put the elements in the horizontal rows starting with He and ending with Cl on the left hand side of their respective columns. Move Se, Br, Te, I, and element No. 85 over to the left hand side of their columns. The "rare earths" from Pr through Ha are retained in an unclassified group in the vertical columns of E_2O_3, EO_2. Then those elements on the left hand side of the vertical columns have atoms or ions of relatively simple structure. Those on the right hand side of the vertical columns are those which have a relatively complex structure.

[2] Hull, Jour. Frank. Inst. Feb. 1 22

[3] Davey, Phys. Rev. **22,** 221 (1923)

[4] McKeehan, Proc. Nat. Acad. Sci. **8,** 279 (1922)

[5] Meier, Göttingen dissertation, (1921)

[6] McKeehan, Proc. Nat. Acad. Sci. **8,** 254 (1922)

[7] Hull, Phys. Rev. **20,** 113 (1922)

nium[8,9] frozen mercury[10,11] and white tin.[12] Altogether, dimensions are available from crystal measurements for the atoms of 44 elements ranging in atomic numbers from 3 to 90. Elements whose atoms pack in the crystal like spheres are considered to be spherical in their effective, or packing, shape. In such cases the radius of the atom is taken as half the distance of closest approach of atom-centers in the crystal. Atoms of the inert gases are assumed to be approximately spherical because the ions of the adjacent alkalies and halogens pack as spheres or as spheres with slight flat spots.[3] Other atoms, because of the crystal structures into which they pack themselves, are considered to be spheroidal, and the major and minor radii are taken as half the "distance of closest approach" in directions corresponding to the major and minor axes of an ellipsoid of revolution.

Elements which tend to revert, upon chemical combination, to the Ni, Pd, Pt type of atoms are supposed to have a relatively complex outer structure. They are the elements which belong on the right hand side of the vertical columns of the older Mendelejeff table.[1] For brevity such atoms will be called "complex atoms." The other atoms, which tend to revert upon combination to the inert-gas type of atom, will be called "simple atoms."

Using the definitions given above the new law is as follows: *The ratio of the radii of any two simple atoms belonging to the same vertical column in the periodic table is the same as the ratio of the radii of any other two simple atoms on the same horizontal lines of the table provided that these atoms also belong to a common vertical column.*

TABLE I

RATIOS OF RADII OF ATOMS OF SIMPLE ELEMENTS

Ar/Ne = 1.57/1.26 = 1.25	Kr/Ar = 1.71/1.57 = 1.09	Ta/V = 1.42/1.32 = 1.08
K/Na = 2.25/1.86 = 1.21	(1) Zr/Ti = 1.62/1.48 = 1.09	W/Cr = 1.36/1.25 = 1.09
Ca/Mg = 1.96/1.61 = 1.22	(2) Zr/Ti = 1.59/1.45 = 1.10	(1) Os/Fe = 1.36/1.23 = 1.11
(1) Ti/Si = 1.48/1.17 = 1.26	Mo/Cr = 1.36/1.25 = 1.09	(2) Os/Fe = 1.33/1.23 = 1.08
(2) Ti/Si = 1.45/1.17 = 1.24	(1) Ru/Fe = 1.34/1.23 = 1.09	Ir/Co = 1.35/1.26 = 1.07
	(2) Ru/Fe = 1.32/1.23 = 1.07	Pt/Ni = 1.39/1.25 = 1.11
	Rh/Co = 1.35/1.26 = 1.07	

In case the elements concerned have two radii, the ratio may be taken either between the major radii or between the minor radii. For instance, Zr and Ti both have simple atoms and both fall in group IV of the periodic table. Mo and Cr both have simple atoms and fall in group VI of the table. The ratio of the major radii of Zr and Ti is 1.09; that of

[8] Kolkmeijer, Proc. Acad. Sci. Amsterdam **25**, 125 (1922)
[9] Hull, Phys. Rev. **20**, 113 (1922)
[10] McKeehan and Cioffi, Phys. Rev. **19**, 444 (1922)
[11] Alsen and Aminoff, Goel. For. Stock. Forh., **44**, 124 (1922)
[12] Marx, Polangi and Schmid, Naturwis. **11**, 256 (1923)

their minor radii, 1.10. The ratio of the radii of Mo and Cr is 1.09. Similar data have been worked out covering the whole range of the periodic table. They are expressed in graphical form in Fig. 1. A few numerical illustrations of the law are given in Table I. It is quite evident from the graphs that the new law does not apply to atoms of "complex" structure. It is worthy of note that the type of crystal structure does not

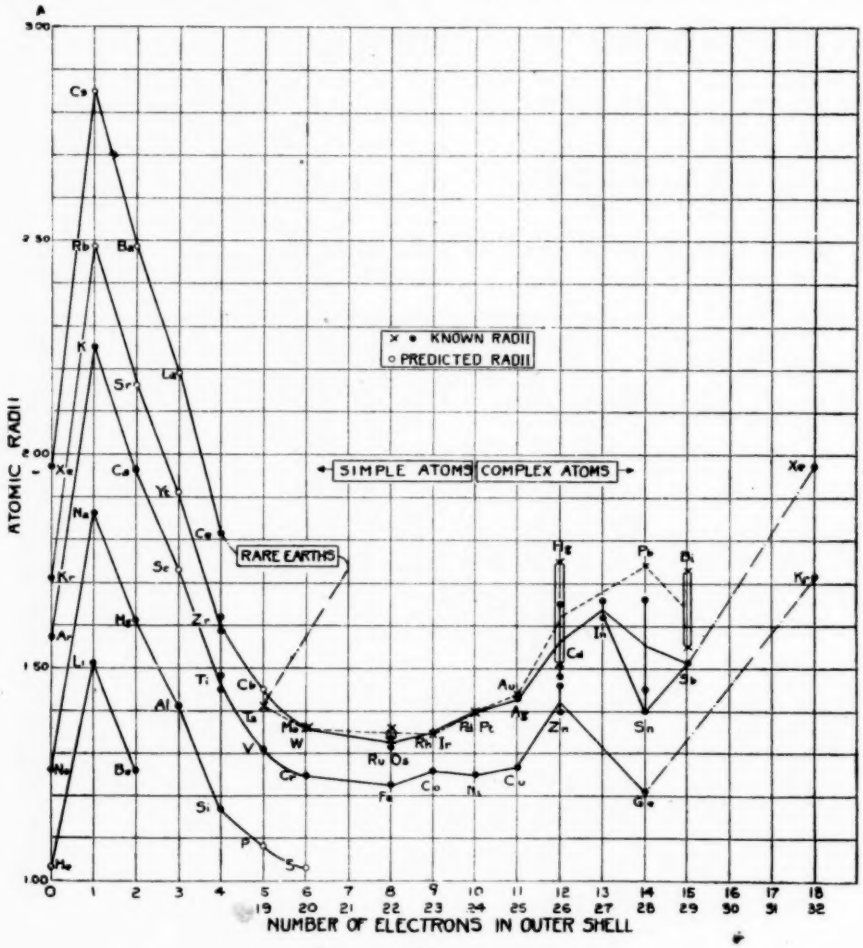

Fig. 1

enter into this law. Ratios may be taken indifferently between atoms which pack together in different crystallographic systems, provided only that the atoms are chosen in accordance with the law.

The new law does not hold for C, using the distance of closest approach in either diamond or graphite. This is not surprising, for there is every evidence that the C atom is tetrahedral in shape. Under such circum-

stances, the word "radius" is of course meaningless. Such an objection does not, however, apply to the same extent to Si, for it has (using Langmuir's terminology) a complete "IIa" shell beneath its valence electrons, thus giving it more nearly a real "radius."

Instead of the radius 1.43 A for Al as given by Hull,[2] the value 1.41 A has been used. This is the radius measured by the writer in some work not yet published on very pure Al. In the case of Ne, the value of the radius, based on the crystal lattice of NaF is 1.15 A. The radii of Na^+ and F^- are, however, quite variable,[3] that of Na^+ in NaI being 1.26 A, so that no great precision can be claimed for the radius assigned to Ne. A radius of 1.26 A for Ne is consistent with the new law in every case.

The new law is not what might have been expected from our ordinary ideas on atomic structure, for it might be imagined that increasing the atomic number would cause a definite increment or decrement in volume. Actual trial shows, however, that, although a few elements show constant differences in radii, this is the exception rather than the rule. The universal rule seems to be that the law for change of volume for any horizontal row of simple atoms is the same as that for any other horizontal row of simple atoms.

The new law makes it possible to predict the radii of certain atoms which have not yet been measured. Such predictions are given in Table II. The graph in Fig. 1 has been extended down to show a "radius"

TABLE II

PREDICTED ATOMIC RADII IN ANGSTRÖMS
(probably accurate to within 2 percent)

P	S	Sc	Rb	Sr	Yt	Cb	Cs	Ba	La
1.08	1.03	1.73	2.49	2.16	1.91	1.45	2.85	2.48	2.19

for He of 1.03 A. This is to be compared with Rankine's value[13] of 1.08 A. The agreement is quite satisfactory, especially in view of the fact that He has a shell of only two electrons, so that it must on the average rotate with its axis in all possible directions in order to give any meaning to the word "radius."

Because of the large number of electrons in the Xe shell, it would be predicted *a priori* that Cs atoms should pack like spheres, thus giving either a hexagonal-close-packed lattice of axial ratio 1.633, or a face-centered-cubic lattice. The density of Cs as computed from the predicted radius is consistent with this idea.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
Schenectady, N. Y.,
December 11, 1923.

[13] Rankine, Phys. Zeit. **11**, 497 (1910); Proc. Roy Soc. **84**, 182 (1910)

ON THE EXCITATION OF THE HELIUM SPECTRUM BY ELECTRONIC BOMBARDMENT

By A. Udden[1] and J. C. Jacobsen

Abstract

Variation in relative intensity of the ortho- and parhelium spectra with the energy of the exciting electrons, 25 to 100 volts.—In the tubes used, electrons were accelerated from a Wehnelt cathode through a platinum grid 1 mm away into a metal box, and the spectrum of the light produced inside the box was photographed. A pressure of about 1mm was used. At the higher voltages, the two spectra were of about equal intensity, but at low voltages the orthohelium spectrum was relatively much the stronger (see Plate I). This is explained by supposing that the orthohelium spectrum is to a large extent due to bombardment of metastable atoms by electrons with energies corresponding to less than 5 volts. A special experiment, however, in which the helium was bombarded by both 5 volt and 21 volt electrons, gave a negative result, no additional light being excited by the slower electrons; but this is not considered as conclusive.

Introduction

As is well known, the arc spectrum of helium contains two complete systems of lines, the ortho- and parhelium spectra, each composed of a principal and two subordinate series. In strong electric fields combination lines appear within each of the spectra while no combination has ever been observed between the ortho- and parhelium terms. According to the theories which have been developed by Bohr, Sommerfeld, Lande and others, the orthohelium lines originate from transitions between stationary states where the two electrons in the helium atom revolve in co-planar orbits, and the parhelium lines from transitions between stationary states with crossed orbits. The fact that no combination has ever been observed between the ortho- and parhelium terms proves that transitions from crossed to co-planar orbits or vice versa are impossible.

By the experiments of Franck and Knipping[2] and Horton and Davies[3] it has been shown that the helium atom has two resonance potentials, 19.5 and 20.3 volts, corresponding to the transference of the atom from the normal state to stationary states with co-planar and crossed orbits

[1] On account of his illness and subsequent decease Mr. Udden has been prevented from taking part in the final writing of this report of our common experiments.

[2] Franck and Knipping, Zeit. f. Phys. **1**, 320, 1920

[3] Horton and Davies, Proc. Roy. Soc. **95**, 408, 1919

respectively. The ionisation potential has been found to be 24.5 volts.[4] By the investigations of Franck[5] it has further been shown that the stationary state with co-planar orbits which has the lowest energy is metastable; when the helium atom has been brought into this state, it can return to the normal state only by impact of electrons or by combining chemically with impurities.

The present investigation was undertaken with the view of obtaining by spectroscopic means some information concerning the excitation of the different quantum steps of the helium spectrum. Such information may be obtained by observing the appearance of the helium lines when excited by electrons of varying velocity. Although we have not succeeded in bringing out all the features claimed by theory, a report of the experiments may be of interest, because it seems to offer a support for the existence of the metastable state of the helium atom.

Experiments

The apparatus was a two-electrode tube with a cathode consisting of a platinum strip coated with calcium oxide, which was fused to copper rods (see Fig. 1); the electrons were accelerated to a platinum grid forming the bottom of a small rectangular metal box open on the side facing the spectrograph. The distance from cathode to grid was about 1 mm.

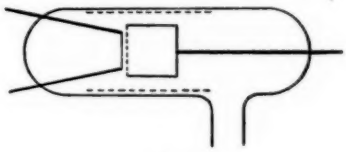

Fig. 1

The metal parts were enclosed in a glass tube consisting of two parts fitting together in a ground glass joint (not shown in the figure) and were sealed into the tube by means of sealing wax. A silver screen, which was connected to the ground, surrounded the grid and cathode and served to protect these from stray fields.

Before making any observation the tube was carefully evacuated, was heat treated as far as possible and the cathode was glowed out for several hours. Helium was then admitted through a U-tube with charcoal immersed in liquid air, which was kept on during the whole experiment. With suitable potentials on the grid a glow appeared in the metal box allowing the helium spectrum to be photographed with exposures

[4] The values here given are corrected in accordance with the recent measurements of the ultra-violet helium series by Lyman, Nature, August 26, 1922

[5] Franck, Zeit. f. Phys. **1**, 154, 1920

ranging from 1 minute to 1 hour. The accelerating potentials (from 25 to 100 volts) were read on a voltmeter, the terminals of which were connected to the grid and the negative end of the cathode. The pressure usually was about 1 mm. The spectrograph was a Hilger glass spectrograph with constant deviation, giving on ordinary plates the region from 3800 to 5200 A in our exposure.

Photographs of the helium spectrum obtained with different accelerating potentials are shown on Plate I. The potential read on the volt-

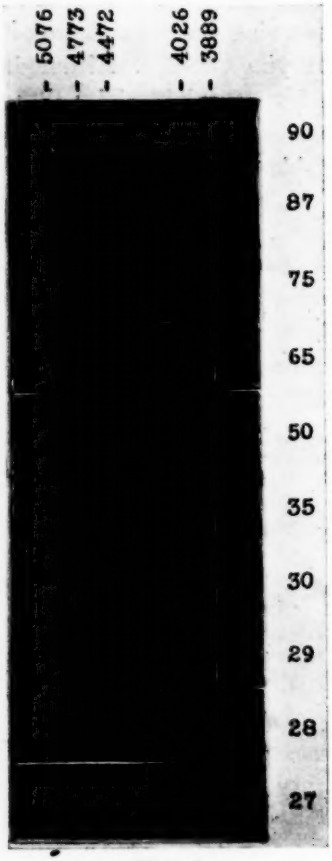

Plate I
Helium spectrum with accelerating voltage 27 to 90.*

meter is indicated opposite the photograph and the identity of the most prominent lines is shown at the top of the figure. At relatively high accelerating potentials (90 volts) the parhelium and orthohelium spectra as a whole appear with the same intensity, but as the potential decreases,

* Wave-lengths should be 5016 and 4713 instead of 5076 and 4773.

the intensity of the parhelium lines is reduced and at a potential of 27 volts the parhelium lines are hardly visible, while the orthohelium lines exhibit a marked intensity at this potential. The time of exposure was chosen according to the intensity of the glow so as to get a suitable impression on the plate; for the lower potentials the time of exposure was about 1 hour. The current varied from 0.1 to 1 milliamp.

The photographs shown on Plate I were chosen from among a number of plates taken with various tubes differing slightly in geometrical design. At a definite voltage the appearance of the spectrum was not always the same but varied somewhat according to pressure and electron current; the voltage given is correct only for certain conditions. A trace of hydrogen, which manifested itself on some of the plates did not seem to be of any influence on the appearance of the helium lines.

The results are somewhat contradictory to those of Rau,[6] Horton and Bailey,[7] Compton and Lilly,[8] Davies[9] and Déjardin.[10] These authors found that the different quantum steps of the helium spectrum were all excited at the same time and especially that no difference could be detected between the voltages for the excitation of the ortho- and parhelium spectra. Whatever the reason may be for this discrepancy, it appears from the photographs on Plate I that a difference in the behavior of the ortho- and parhelium spectra, when excited by relatively slow electrons, is established beyond any doubt, the orthohelium spectrum coming out much more strongly than the parhelium spectrum.

Discussion

The most reasonable explanation of the experimental results is to be looked for in the existence of the metastable state of the helium atom. When a helium atmosphere is bombarded by electrons of sufficient velocity, at least part of the collisions will result in the formation of atoms in the metastable state and these atoms can only return to the normal state by impact of electrons or by combining chemically with impurities present. In this way a state of equilibrium is reached where a certain number of atoms in the metastable state are present, depending upon the number and velocity of the electrons and the amount of impurities. If the electrons have a high velocity practically all collisions with metastable atoms will result in ionisation. When the ionized atom returns to

[6] Rau, Würzb. Phys. Med. Ges. Ber. Feb., 1914
[7] Horton and Bailey, Brit. Ass. Rep. 1919, 153
[8] Compton and Lilly, Astrophys. J. **52**, 1, 1920
[9] Davies, Proc. Roy. Soc. **100**, 599, 1922
[10] Déjardin, Journ. de Phys. **4**, 121, 1923

the normal state the parhelium lines may be emitted just as well as the orthohelium lines so that the spectrum emitted contains the parhelium and orthohelium lines with the same intensity on the average.

If on the other hand electrons with low velocities are being used, the metastable atoms present may give rise to an increased intensity of the orthohelium spectrum. If a metastable atom collides with an electron of say 4 volts the atom will ordinarily be brought into a second stationary state with co-planar orbits and the spectrum emitted during the return of the atom to the metastable state, which is the only one possible, can contain only orthohelium lines. When a helium atmosphere is bombarded by electrons with velocity of 26-27 volts, electrons with low velocity will be present in considerable number and this fact in connection with the existence of the metastable state of the helium atom may probably offer an explanation of the phenomenon observed.

If this explanation is correct the following experiment ought to be possible. Let a helium atmosphere be bombarded by electrons with a velocity of say 21 volts so that a number of metastable atoms are formed while the intensity of the visible helium spectrum at least with moderate electron currents is very small. If from a second cathode electrons with a velocity of say 5 volts are supplied this ought to result in an increased intensity of the visible helium spectrum. We have carried out this experiment with an apparatus where electrons from two separate cathodes were sent into a metal box, the sides of which consisted of platinum gauze, the direction of the two electronic streams being at right angles to one another.

The result of the experiments has so far been negative. It was not found possible to excite the helium lines by simultaneous bombardment with electrons of two different velocities of which one was about 21 volts and the other one much lower. But even if we have not been able to establish a definite proof of the explanation given above of the difference in the behaviour of the ortho- and parhelium spectra, the question can not be regarded as settled by such a negative result. The problem is to find the proper conditions.

Acknowledgments are due to Prof. N. Bohr for his kind interest throughout the entire course of the work.

UNIVERSITY INSTITUTE FOR THEORETICAL PHYSICS,
COPENHAGEN, DENMARK,
October, 1923.

INTENSITY RELATIONS IN THE HELIUM SPECTRUM

C. B. Bazzoni and J. T. Lay

Abstract

Low-voltage arc in pure helium.—Inside a blown quartz tube, electrons from a tungsten spiral were accelerated into the equipotential space inside a hollow copper anode. Unusual purity was obtained by heating the anode red hot by high frequency induction to remove gases, in addition to other precautions. *Minimum operating potential* was found to be 21.5 volts, just above the resonance potential. The relative importance of the ionizations at 20.5 and at 25.5 volts depends on the pressure and current density; after the current has risen to a high value the 25.5 point is obscured, indicating probably a decrease in the proportion of normal atoms under the increased radiation. *Change in relative intensity of arc spectrum lines with voltage* was studied for 25 to 85 volts, using the neutral wedge method of Nicholson and Merton. The crossed orbit lines λ 4437 (*1P—4S*), λ 4387 (*1P—4D*), λ 4922 (*1P—3D*), λ 5016 (*1S—2P*) all increase with voltage, though not uniformly; while the coplanar lines λ 4713 ($1\pi-3\sigma$), λ 5875 ($1\pi-2\delta$), λ 4471 ($1\pi-3\delta$) all diminish to a minimum at about 50 volts.

SOME of the earliest observations on intensity relations in the helium spectrum as affected by energy considerations were made visually by Richardson and Bazzoni[1] who, in the course of experiments on the successive stimulation of lines under increasing energy of bombardment found that, while most of the lines increased steadily in intensity with the bombarding voltage, line λ4713 of the sharp series of orthohelium increased to a maximum soon after its appearance, decreased to faintness at 40 volts and then increased again. The blue line 4472 ($1\pi-3\delta$) was found to require about $\frac{1}{2}$ volt and the blue line 4713 ($1\pi-3\delta$) about $\frac{1}{4}$ volt more energy for stimulation than the yellow line 5875 ($1\pi-2\delta$).

These facts seemed of sufficient importance to warrant further investigation which was undertaken by Bazzoni and reported on in a paper read before the Amer. Phil. Soc. in April, 1921.[2] In this work the spectrum was produced by suitably accelerated thermions in a field-free space and was photographed through Hilger neutral tinted wedges. The results obtained at the time were not of a positive character and after a reconstruction of the apparatus the work was repeated beginning in October, 1922. The present paper contains a report on the first series of results obtained with the new apparatus.

[1] Richardson and Bazzoni, Nature **88,** 5 (1916)

[2] Read in full but published by title only.

Fig. 1 is a sketch of the discharge chamber, which is of blown quartz, and was constructed by the Thermal Syndicate, New York. A window of optical quartz is fused on at *W*. Projecting downward is a tube *O* closed at the bottom which can be inserted into a Thermos flask filled with liquid air. The cathode *C* is a tungsten spiral which can be replaced by removing the stopper *F*. This stopper is accurately ground and is vacuum tight but can be sealed into position with hard wax when desired. The anode *K* is a flat pill-box of copper having numerous holes in the face opposite the filament *C* forming a grid, and a rectangular opening in the side opposite the quartz window *W* for spectroscopic examination. This box can be moved back and forth by means of a piece of iron sealed into a quartz stem wired to it but in use it was found easier to adjust the filament distance by moving the filament. This distance was generally kept as short as possible.

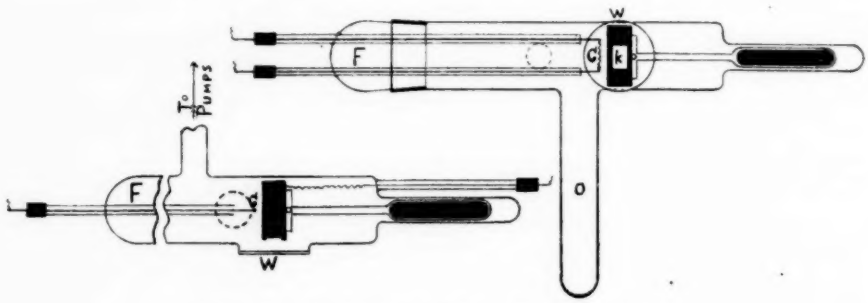

Fig. 1. Discharge chamber, of blown quartz.

The device was set up so that the coil of an induction furnace could be slipped over it and the box brought to a brilliant red heat and held so as long as desired. A Hilger constant deviation spectrometer provided with a camera attachment and with Hilger neutral tinted wedges of suitable density in front of the slit, was used in analyzing the light from the arc. The spectrometer slit was set as close as possible to the quartz window. The lenses and prism of this instrument and also the wedges were of glass.

The helium used was from a lot very kindly supplied by Dr. R. B. Moore of the Bureau of Mines, the original source being natural gas. This was purified in an apparatus and by a procedure identical with that described by Richardson and Bazzoni.[3] Hydrogen can be burned out by sparking in an atmosphere of pure oxygen over phosphorous pentoxide. The excess oxygen and other gases are then removed by charcoal in liquid

[3] Richardson and Bazzoni, Phil. Mag. **34**, 285 (1917)

air and, since the operations are controlled by mercury traps instead of stopcocks, a final liquid air trap is inserted to remove the mercury vapor. The whole arrangement was evacuated by a Langmuir metal condensation pump backed by large oil pumps. The pressure could be measured with a McLeod gauge suitably placed with reference to the last liquid air trap.

After the quartz device had been held at a red heat for a sufficient time, the copper box had been heated with the induction furnace and the filament had been glowed out, helium of the most unusual purity could be produced and worked on for a long time. Even after six hours of continuous use with filament glowing and potentials applied, absolutely no trace of any contamination from hydrogen or mercury could be detected spectroscopically. This degree of purity could only be obtained by the most stringent heat treatments. If the box was not held at a red heat over liquid air and charcoal for a long enough time mercury lines appeared after a few minutes use.

The driving potential was obtained from a potential divider across a 110 volt battery of high capacity storage cells and was measured by a Weston standard voltmeter. The filament current was drawn from a similar 50 volt battery and was adjusted through a set of resistances in parallel. The thermionic current was measured with Weston microammeters or milliammeters as required.

The primary purpose of the investigation at this stage was to study the intensities of the lines of the spectrum as functions of the driving potentials but since the helium was recognized to be of a degree of purity seldom obtained it was thought desirable to make certain preliminary observations on the critical potentials of arc production in it. Previous experiments as well as considerations of theory had led the authors to believe that an arc and the associated ionization can be maintained in pure helium at any potential above the first resonance potential but not at a lower potential. It seemed probable that experiments of other investigators leading to very low values of the potential for maintaining the arc were conducted in tubes containing metal parts which could not be heated in the clean-up, wherefore mercury vapor or hydrogen might have been present in sufficient quantities to have produced, through radiation or contact, a disturbance of the normal helium atoms.

It was found impossible, when proper conditions of cleanliness had been obtained, to hold an arc in our purest specimens of gas below 21.5 volts, the transformation voltage for producing co-planar helium. On the other hand the slightest trace of contamination, especially of mercury, made it possible to carry a faint but definite glow down to 12

volts. If the copper box were allowed to stand in the apparatus without liquid air (therefore in an atmosphere of mercury vapor) over night it would absorb sufficient mercury to produce this effect, which could subsequently be eliminated only by bringing the box to a distinct red heat over liquid air. These observations strengthen the idea that if there is nothing in the arc space except helium, an arc cannot be held below the first resonance point of the gas. It is probable that stimulated mercury atoms can transfer energy to helium atoms by contact or otherwise as observed by Franck and Cario[4] with mercury and hydrogen.

In the absence of mercury a marked ionization below 25 volts could be obtained only under heavy bombardment or with high pressures. Fig. 2, Curve A is characteristic of runs under moderate bombardment

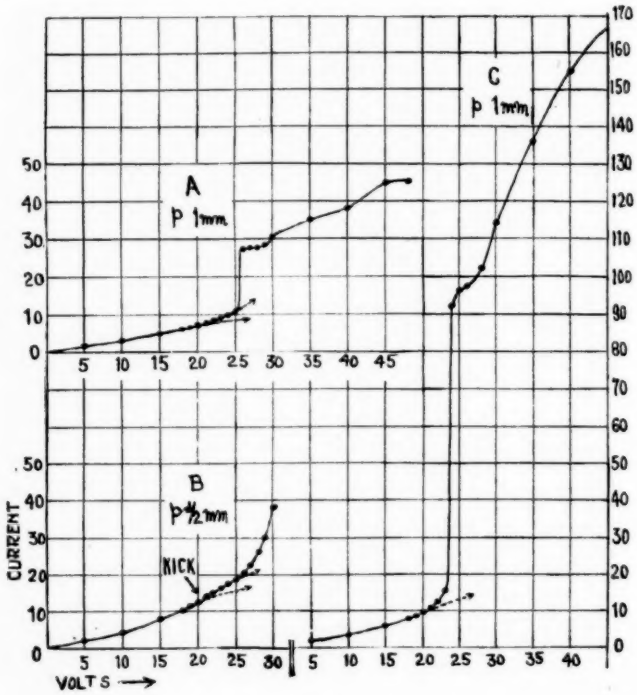

Fig. 2

(pressure 1 mm). Curve B is still more typical (pressure ½ mm). Here the ionization which sets in at 20.5 volts is relatively inconspicuous compared with that which starts around 25.5 volts. Curve C shows the modification produced under heavy bombardment. The sharp rise in the neighborhood of 23 volts on this curve is due to an alteration of the

[4] Franck and Cario, Zeits. f. Physik **11**, 161 (1922)

space-charge and is not associated with an ionization point. Once this "kick" has taken place the 25.5 volt point, the generally accepted ionization point of normal helium, is obscured. This supports the hypothesis of Richardson and Bazzoni[1] that normal helium is altered in a field of intense radiation to a form of less stability with a lower ionization point. The curves of Fig. 3 illustrate this point. Here a tungsten filament was used with the heating currents indicated at the ends of

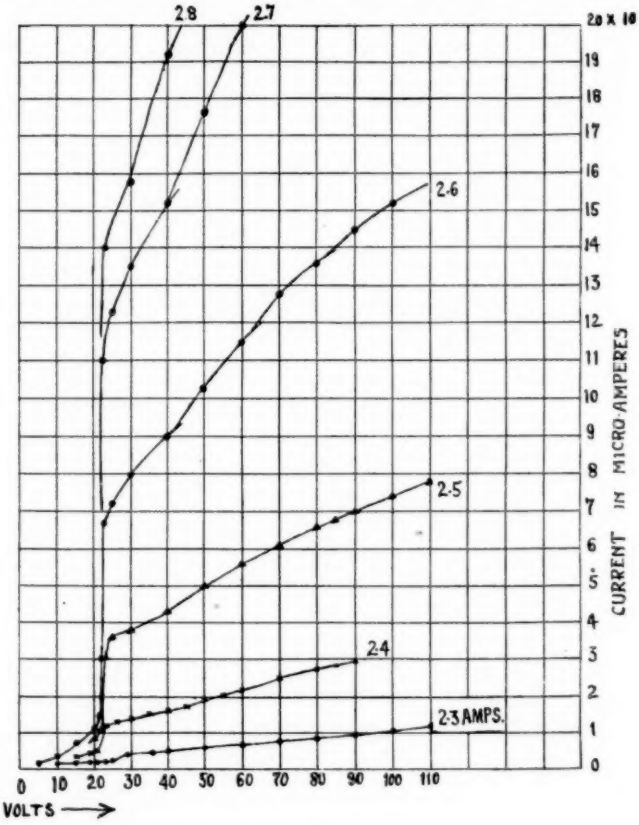

Fig. 3. Current curves for various heating currents of the tungsten filament.

each curve. Additional ionization points are observable on these curves at multiples of 20 volts including 80 volts, the supposed potential of double ionization. Throughout this work whenever there was a glow a spectrum could be observed which consisted of the full visible spectrum of helium including both series.

These observations, made at various times during the past year, are in accordance with those published by Desjardin[5] and also with those given by Richardson and Bazzoni.[3]

[5] Desjardin, Jour. Phys. et Rad., April 1923

After the completion of these preliminary observations attention was turned to the intensity measurements.

The method of the neutral tinted wedge for spectro-photometry has been most carefully worked out, both in practice and in theory, by Nicholson and Merton[6] who applied it in investigations of the fine structure of lines. A wedge of Schott neutral tinted glass is cemented to a similar wedge of clear glass to form a block of rectangular section with a certain ratio of transmission between that of the thin edge, which is clear, and that of the thick edge. This ratio depends on the thickness of the wedge and on the composition of the melt from which the glass is made. When the wedge is in front of the slit the heights of the images of the various spectrum lines on the plate will be in proportion to the intensities of the lines. In our work we followed the method of Nicholson and Merton—enlarging the original $3\frac{1}{4}$ by $4\frac{1}{4}$ plates on to 8 by 10 plates and printing these plates on contrast paper through a half-tone screen cross-lined 100 lines to the inch, thus obtaining the line images made up of small dots. To determine the height of a line it is then merely necessary to locate the last visible dot, which is a fairly definite procedure but little affected by personal error. It is of course understood that any attempt to compare the intensities of lines in different parts of the same spectrum, or in different spectra, is complicated by considerations of the variation of transmission of the wedge for different wave-lengths and by the variation in sensitivity of the photographic plate in different parts and for different wave-lengths. These complications can to some extent be corrected for by preliminary determinations of the wedge transmission and of the color sensitivity of the plate but variations of emulsion on the same plate are entirely accidental. Results obtained by this method must therefore, to be precise, depend on measurements made on a very small area of the emulsion where it may be supposed uniform—as, for instance, in studies of the fine structure of a single line such as Nicholson and Merton made. Nevertheless, for work which is not carried to a fine point, experience shows that it is safe to assume the emulsion on selected plates properly handled to be uniform excepting at the edges, intensity curves from the same source on different parts of the same plate or even on different plates of the same lot being indistinguishable by the methods used. The wedge measurements are furthermore free from certain sources of error unavoidably associated with intensity determinations through photometry and have obvious advantages in convenience.

[6] Nicholson and Merton, Phil. Trans. A **216,** 459, 1916, and A **217,** 237, 1917

In making experiments to produce plates to show intensity variations with voltage it is necessary to keep both the pressure and the bombardment current constant. This, in practice, is not easy—the pressure in particular being subject to interesting and probably significant changes under the action of the discharge. Fig. 4 (a), (b), (c), (d) and (e), are spectra from a plate secured under satisfactory conditions. These spectra were taken with a fixed thermionic current under potentials respectively of 25, 35, 55, 75, and 85 volts. The exposures were in each

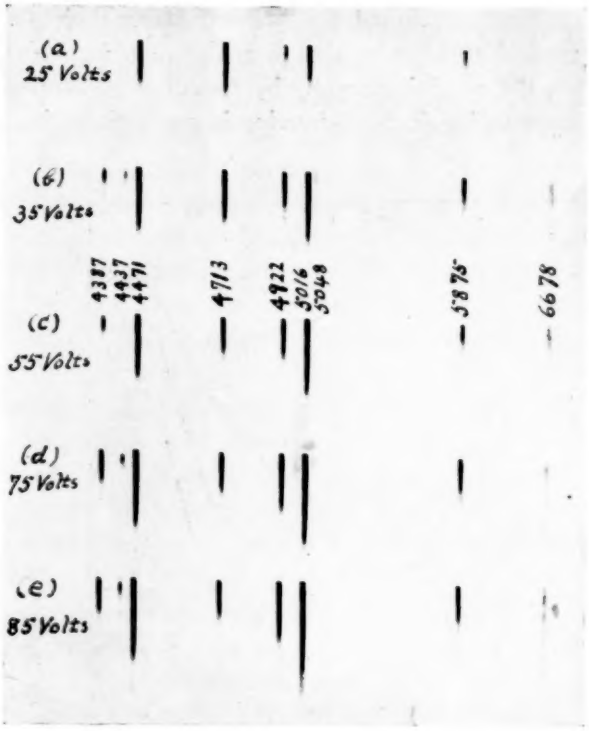

Fig. 4. Spectra obtained with potentials 25 to 85 volts.

case one half hour, the arc being maintained in helium at 0.33 mm pressure by a bombarding current of 60 milliamperes which was kept constant by altering the filament current. The tungsten filament carried 2.7 amperes at 25 volts driving potential and 2.4 amperes at 85 volts. The utmost care having been exercised in preparing the helium and in cleaning up the apparatus the gas remained spectroscopically pure throughout the work. The plate was a Wratten and Wainwright panchromatic, specially backed.

The lines which are clearly measurable on this plate are

crossed orbit			coplanar		
S	4437	$1P-4S$	S	4713	$1\pi-3\sigma$
D	4387	$1P-4D$	D	5875	$1\pi-2\delta$
D	4922	$1P-3D$	D	4471	$1\pi-3\delta$
P	5016	$1S-2P$			

Those in the first column belong to the singlet series ascribed to parhelium; those in the second column belong to the series of doublets ascribed to orthohelium. It will be recalled that according to recent theory normal helium atoms (parhelium) have their two electrons moving in crossed orbits and that a metastable form (orthohelium), produced from the normal generally by radiation absorption or impact, is supposed to have its electrons moving in coplanar orbits, one outside the other.

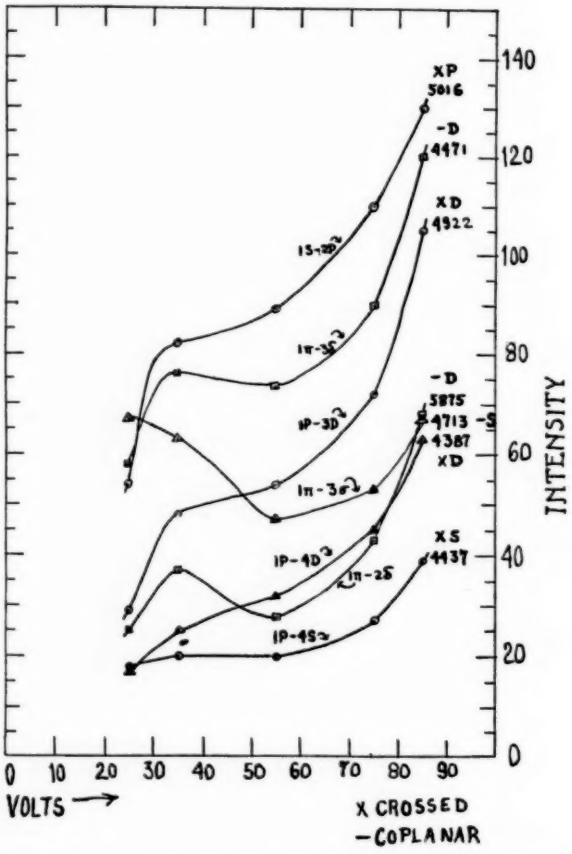

Fig. 5. Intensity of various lines as a function of the voltage.

When the intensities of these lines, as determined by measuring their heights, are plotted against the driving voltages the curves shown in Fig. 5 are obtained; one curve for each of the seven lines. It will be observed that there is a marked difference in the behavior of the lines of the coplanar helium as compared to the lines of crossed orbit helium in that the coplanar lines all show a definite drop in intensity between 35 and 55 volts. All the lines of both series, with the exception of 4713, increase in intensity between 25 and 35 volts and again above 55 volts. The rate of increase is apparently greater above 75 volts than between 55 and 75.

Although 55 volts is the potential for the appearance of the enhanced or spark line 4686, no trace of this line was found at any potential up to 110 volts. The development of the spark (double ionization) lines, of which 4686 is the first, as well as the development of the band spectrum requires a pressure adjustment not suitable for the clearest production of the arc lines.

Line 4713 is apparently somewhat anomalous in that its intensity diminishes above 25 volts and does not increase notably until in the neighborhood of 80 volts. This observation is in accordance with the one made visually by Richardson and Bazzoni and reported in Nature in 1916.

With reference to the potentials of appearance of these lines—no lines can be observed visually or on the photographic plate even with exposures of 18 hours before a glow develops in the tube. The appearance of the glow is associated with some alteration of the space charge evidenced by a rise in current and a drop in potential across the arc—the kicks of the instrument needles being generally a safe indication that the glow has formed. In the particular sample of gas from which the above photographs were made the glow appeared with no observable kick at 22 volts. With increasing voltage a marked kick occurred at 32 volts accompanied by the formation of a heavy glow behind the cathode. On lowering the potential a reverse kick took place at 28 volts, the voltage rising to 29. On again reaching 28 volts another kick occurred, the glow shrinking behind the cathode but remaining in the box. At 23.5 volts the glow disappeared from the box without any definite instrumental kicks. The glow showed a change in color with change in voltage, being a weak blue at 35 volts, a greenish or robin's egg blue at 55 volts and an intense bright blue at 75 volts and above. As far as a cursory observation showed the green and yellow lines appeared and disappeared together but since the observations made in 1916 indicated definitely that the 3δ lines required a higher voltage to excite them than did the 2δ lines the examination is to be repeated with proper refinements.

Little can be said of the significance of the results here given since theories of atomic structure are not yet sufficiently developed to explain the facts shown. Coplanar helium being presumably produced by impacts of 20.5 to 21 volts energy or by the absorption of a corresponding radiation we might possibly expect a greater number of these atoms to be present at voltages in the lower twenties which might lead to an intensity maximum there and to a minimum at somewhat higher voltages, as is observed. The number of normal atoms being reduced as the coplanar ones are formed we might also expect a decrease in the rate of increase of intensity of the normal lines during the period of formation of the coplanar atoms. This is seen to be roughly the case.

The value of these observations would be greater if they were extended further into the ultra-violet. The experiments are being continued along these lines, using quartz wedges, lenses and prisms.

Since this work was completed an abstract has appeared by A. L. Hughes[7] reporting on a similar investigation made on helium using a similar method. The results given by Hughes are in general agreement with those obtained by us.

RANDAL MORGAN LABORATORY,
UNIVERSITY OF PENNSYLVANIA,
September 15, 1923.

[7] Hughes and Lowe, Phys. Rev. **21**, 714 (1923)

LIGHT SENSITIVITY OF CUPROUS OXIDE AND OF SELENIUM

VOLA PRICE BARTON

ABSTRACT

Three photo-electric effects for certain samples of Cu_2O and Se as functions of wave-length.—Light from a tungsten lamp or iron arc was dispersed by a quartz spectrometer. Measurements with a thermocouple enabled all results to be reduced to unit light intensity. The observations agree well with previous results obtained with various samples. (1) *Decrease of resistance* was measured for the range 3900 to 6000 A for Cu_2O, maximum at 4600 A, and for 4300 to 9300 A for Se, maximum at 7000 A. (2) *Photo-electrolytic potential* was found to exist for both back (contact with air) and front (contact with distilled water) illumination, and was measured in the case of front illumination for the range 2700 to 5500 A for Cu_2O (maximum at 3500 A, upper limit about 5600 A), and for 2700 to 9000 A for Se (maximum at 5700 A, upper limit about 9500 A). The effect was positive and proportional to the intensity I for Cu_2O and to $I^{\frac{1}{2}}$ for Se. (3) *Photo-electric wave-length limit* was found by the use of absorption screens to be at about 2570 A for Cu_2O and at 2260 A for Se. For both Cu_2O and Se, all samples showed the same photo-electric limits and those which showed a change of resistance also showed the photo-electrolytic effect, but not vice-versa.

INTRODUCTION

IN the present investigation, three photo-effects have been measured on the same sample, since different samples have been found to vary greatly in their sensitivity. The photo-effects that have been measured are: first, the change in the electrical resistance produced by light; second, the change in the potential of the substance produced by light when the substance is one of the plates in an electrolytic cell, i.e. the photo-electrolytic effect; and third, the photo-electric effect.

APPARATUS AND METHOD

For determining the change in the electrical resistance produced by wave-lengths 6000 to 4000 A for Cu_2O, and 9000 to 4000 A for Se, a quartz spectrometer, as described by A. H. Pfund,[1] was used. The source of light was a tungsten lamp of 32 c.p. A water cell was inserted to cut out the strong heat rays. An orange glass screen was used as a shutter for wave-lengths shorter than 4650 A, to reduce the effect of scattered light.

[1] A. H. Pfund, Phys. Rev. **7**, 289, 1916

In measuring the change of resistance produced by different wavelengths of light, the Wheatstone's bridge was balanced as closely as possible with the resistance cell, not illuminated, as the unknown resistance. The reading of the galvanometer was taken. Then, by means of the spectrometer, a small region of the spectrum was allowed to fall on the substance, and the steady deflection of the galvanometer was read. The change of resistance was found to be independent of the length of time of illumination, unless that time was exceedingly short. The difference between these galvanometer readings was proportional to the change of resistance of the substance illuminated, as it was experimentally proved that for the galvanometer and resistances used, the deflection was proportional to the change of resistance in one arm of the bridge, the change being small in comparison to the total resistance. The substance being investigated was then replaced by a thermocouple connected to another galvanometer, and the relative intensity of the different portions of the spectrum was obtained. Pfund[1] in his investigations on Cu_2O and Nicholson[2] in his investigations on Se, showed that for any monochromatic portion of the spectrum for which the light is not transmitted by the substance, the change in resistance is porportional to the square root of the intensity of the incident light. Using this fact, the change in resistance produced by equal light intensities of the various regions of the spectrum was obtained.

For determining the photo-electrolytic effect produced by the different regions of the spectrum in the range 8700 to 2500 A, the same quartz spectrometer was used, but the source of light was an iron arc. The substance to be investigated was sealed into the side of the glass cell, as

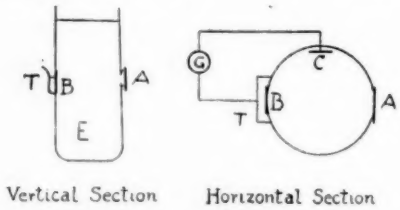

Fig. 1. Photoelectrolytic cell.

shown at *B* in Fig. 1, opposite a quartz window *A*. Great difficulty was experienced in obtaining a good electrical contact to *B*, but this was finally overcome by sealing a small copper sheet *T* directly behind *B*, and filling the space between the copper and *B* with mercury. The other electrode of the cell was in some cases a sample of the same substance as

[2] P. J. Nicholson, Phys. Rev. **3**, 1, 1914

B, sealed into the side of the tube in such a position that the light could not reach it; in other cases a platinum wire or zinc strip immersed in the solution. The solution *E* was distilled water when working with Cu_2O, whereas a few drops of nitric acid were added to the distilled water when working with Se. The two electrodes were joined to the terminals of a high resistance galvanometer *g*.

In measuring the photo-electrolytic effect as a function of wave-length the cell was exposed to the different regions of the spectrum by the quartz spectrometer, and the corresponding throws of the galvanometer were obtained. These throws were porportional to the change in potential produced in the substance. The thermocouple replaced the electrolytic cell after each reading and thus the relative intensities of the incident light at each reading were determined.

To determine the relation between the change in potential produced, and the intensity of the source, the unresolved radiations of a 32 c.p. tungsten lamp was focussed on the specimen. By means of a rotating sector, the intensity was reduced consecutively to ½, ¼ and ⅛ of its total intensity, and the corresponding changes in potential were noted by the galvanometer readings. The results are given in Table I.

TABLE I

Change of potential as a function of intensity of the source

Relative intensity I	Cu_2O dp(obs.)	Cu_2O dp/I	Se dp(obs.)	Se $dp/I^{\frac{2}{3}}$
1	20	20	48.3	48.3
½	10.05	20.1	32.2	51.1
¼	5.2	20.8	23.85	60.1
⅛	2.7	21.6	14.86	59.4

It was shown that for the unresolved radiation, the change in potential produced is proportional to the intensity of the radiation in the case of Cu_2O, and is proportional to the two-thirds power of the intensity in the case of Se. It is assumed that the same law holds for the monochromatic radiations that are not transmitted by the substance. Using this relation, the change in potential produced by equal light intensities of the various regions of the spectrum was obtained.

The apparatus used for determining the longest wave-length that will cause a photo-electric effect of the substance is indicated in Fig. 2. The photo-electric cell was enclosed in an earthed tin case, which was connected by a brass pipe to the brass case containing the electrometer. A small hole was cut in the tin case to allow the light to fall on the cell. The source of light was an aluminium spark when working with Cu_2O,

and an iron arc when working with Se. This light was focussed on the substance in the cell by means of a quartz lens. In determining the long wave-length limit that will cause the photo-electric effect, screens of various thicknesses of glass were used, and when that screen was found

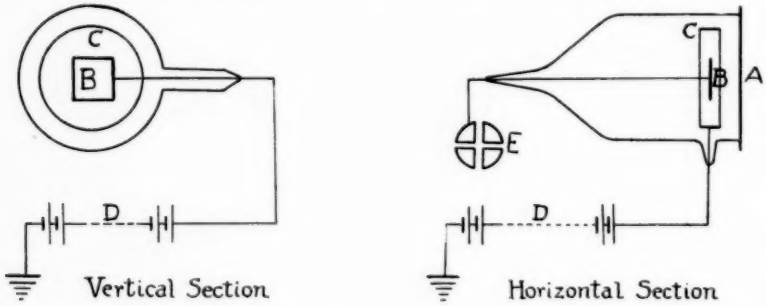

Fig. 2. Photo-electric cell. *A*—Quartz window; *B*—Cu_2O or Se; *C*—Copper cylinder; *D*—Battery of 112 volts; *E*—Electrometer.

which would give a very small deflection of the highly sensitive electrometer, the transmission spectrum of that screen was taken and the shortest wave-length that it transmitted was the longest wave-length that would cause the photo-electric effect of the substance.

Results for Cuprous Oxide

The observed change of resistance of Cu_2O produced by radiations of different wave-lengths in the region 6000 to 3900 A was in good accord with the work done by A. H. Pfund.[1] The final results are shown in Curve I, Fig. 3 in which the ratio of the change of resistance to the square-root of the relative intensity of the radiation is plotted against the corresponding wave-length of light. It will be noted in the graph that there is a slight maximum at 4600 A.

The effect of wave-length on the change of potential of the Cu_2O in an electrolytic cell had been observed by Pfund and E. Karrer, but the results were never published. The readings taken in this investigation confirm their results. They are shown in Fig. 4 in which the change of potential is plotted against the corresponding wave-length in Curve I, and the ratio of the change of potential to the relative intensity is plotted against the corresponding wave-length in Curve II. It will be noted in Curve II that there is a maximum effect at about 3500 A, and that the effect continues throughout the ultra-violet to 2600 A, that is, as far as was investigated.

This potential effect was also observed when the back of the Cu_2O plate was illuminated, that is, when the light did not pass through the

electrolyte, but fell on that face of the Cu_2O plate which was in contact with the air. Stray light was excluded from the front face, and the sample was opaque to all rays except the red.

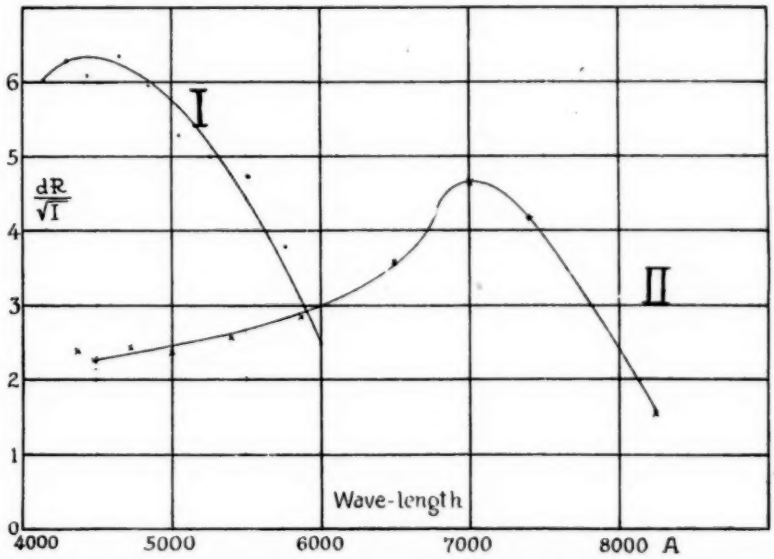

Fig. 3. Change of resistance of Cu_2O (I) and of Se (II) for light of various wave-lengths.

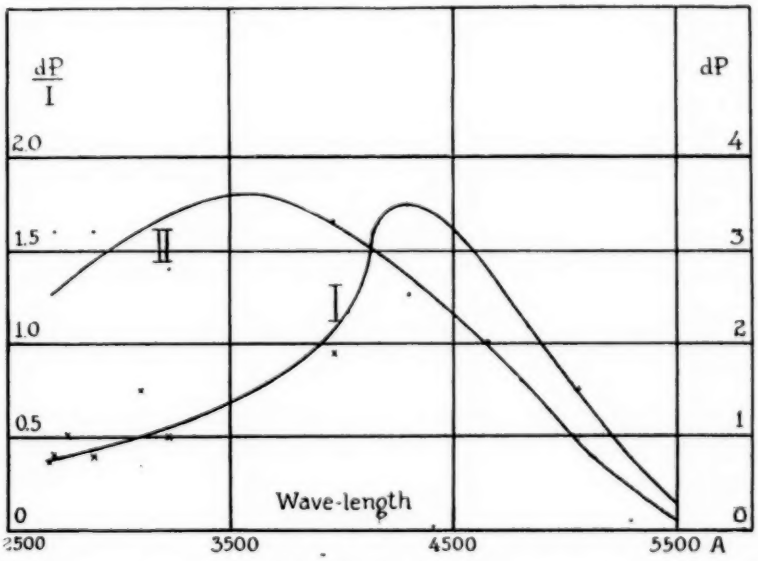

Fig. 4. Change of potential of Cu_2O (I) and Se (II) in an electrolytic cell for light of various wave-lengths.

The absolute magnitude of the potential effect, for front illumination, was determined by connecting the galvanometer to a potentiometer. It was found that the change of potential produced by 3500 A of intensity as obtained from the iron arc, was of the order of magnitude of 10^{-5} volts.

T. W. Case[3] has investigated the effect of light on one electrode of a cuprous oxide voltameter, with copper formate as the electrolyte. In the unresolved radiation of sunlight, he obtained 0.11 volts for the full intensity. But in his work he found that the illuminated Cu_2O plate has its potential lowered. In the present investigation, the illuminated Cu_2O plate was made positive as the result of illumination, the current flowing from the plate to the dark electrode through the external circuit.

R. A. Millikan[4] records the long wave-length limit for copper oxide to be 2535 A with a possible error of 50 A. The long wave-length limit as obtained in the present investigation was 2572 A.

Three pieces of Cu_2O were investigated. They showed the same long wave-length limit for the photo-electric effect, and the same characteristic photo-electrolytic action; but, even though a particular specimen showed a large photo-electrolytic action, it did not, in two cases, show a measurable change of resistance with exposure to light. The mode of preparation of the Cu_2O samples was that described by A. H. Pfund.[1]

Results for Selenium

The observed changes of resistance of Se produced by radiation in different regions of the spectrum in the range of 9000 to 4000 A are in good accord with the results obtained by Nicholson.[2] The final results are shown in Curve II, Fig. 3 in which the ratio of the change of resistance to the square-root of the relative intensity of the radiation is plotted against the corresponding wave-length of light. It will be noted in the graph that there is a sharp maximum at 7000 A.

The change of potential of the Se in an electrolytic cell when the other electrode is platinum has been observed by Minchin.[5] In the present investigation a very much larger effect was observed when the other electrode was a strip of zinc; but this was probably due to the smaller internal resistance of the cell when the large zinc electrode was used. The results for a cell with Se and Zn as electrodes, in distilled water with a few drops of nitric acid added, are recorded in Fig. 5. Curve I shows the relation of the change of potential to the corresponding wave-lengths. Curve II shows the relation of the ratio of the change of potential divided

[3] T. W. Case, Am. Electrochem. Soc. Trans. **31**, 351, 1917
[4] R. A. Millikan, Phys. Rev. **7**, 18, 1916
[5] J. M. Minchin, Phil. Mag. (5) **21**, 207, 1891

by the two-thirds power of the relative intensity of the radiation to the corresponding wave-lengths. Care was taken that the light did not fall on the zinc. The direction of the current obtained was from the illuminated Se to the dark electrode through the external circuit, that is, the Se is raised to a higher potential, by the action of the light. It will be noted from Curve II that there is a decided maximum at about 5700 A.

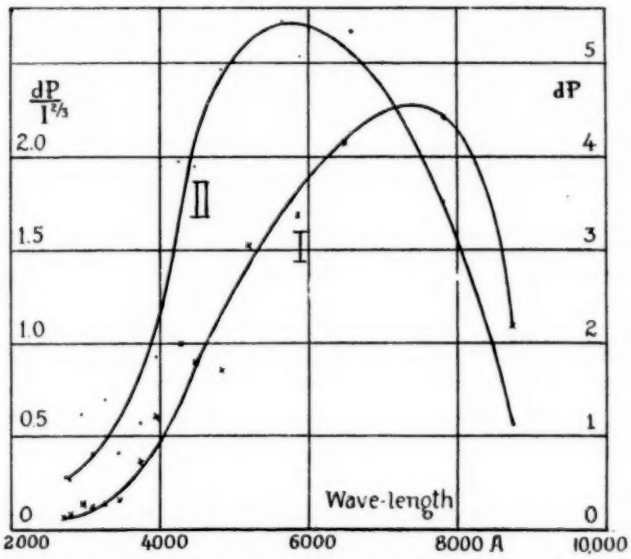

Fig. 5. Change of potential of Se in an electrolytic cell with Zn as the other electrode. Curve I gives dP; Curve II, $dP/I^{\frac{2}{3}}$.

The long wave-length limit as obtained for Se was 2260 A.

Three pieces of Se were investigated. They showed the same long wave-length limit for the photo-electric effect, and the same characteristic photo-electrolytic action, but although the three specimens showed a large photo-electrolytic action, only one showed a measurable change of resistance with exposure to light. The mode of preparation of the Se samples was that described by A. H. Pfund.[6]

Discussion

It has been the purpose of this paper to observe the above-mentioned three photo-effects on the same sample, with a view to aiding in the theoretical interpretation of these and other experimental facts.

The fact that for both Cu_2O and Se, the resistance effect, the photo-electrolytic effect, and the photo-electric effect begin at increasingly short wave-lengths in the order mentioned, indicates (1) that least

[6] A. H. Pfund. Phys. Rev. **28**, 324, 1909

energy is required to simply excite the electrons (assuming Thomson's doublet theory of resistance, since it was found to explain some of the experiments of A. H. Pfund),[1] (2) that a greater amount of energy is required to remove an electron from the substance, and (3) that the greater the dielectric constant of the medium surrounding the substance the less the amount of energy necessary to remove the electron. It is of interest to note that the photo-electric effect of Cu_2O begins at approximately 2570 A and that the ratio $-dR/\sqrt{I}$ begins to decrease at approximately 2800 A (according to Pfund's[1] work in the ultra-violet), having been steadily increasing up to this point. That these two effects should occur at the same wave-length is what would be expected on Thomson's doublet theory of resistance, due to electrons being ejected completely from the substance.

In conclusion, I desire to express my appreciation to Professor Ames and to the entire graduate Physics department of the Johns Hopkins University for the interest taken in the work and to William H. Crew for making the diagrams. I especially want to thank Dr. Pfund, who suggested the problem and so cheerfully aided me in every way.

JOHNS HOPKINS UNIVERSITY,
May, 1923.

A DETERMINATION OF THE DIELECTRIC CONSTANTS OF FIVE GASES BY A HIGH FREQUENCY METHOD

By Edwin C. Fritts

Abstract

Dielectric constants of hydrogen, oxygen, nitrogen, air, and CO_2.—Special cylindrical gas condensers were constructed so as to have a minimum of solid dielectric in the field, and the small capacities were measured by the method of heterodyne beats, originally used by Hyslop and Carman. A photographic record of the beats on a moving film was secured, one side of the wedge slit being fastened to a tuning fork and the other to the diaphragm of a telephone actuated by the beats. The results reduced to 1 atm. at 0°C, accurate to about one per cent of the difference from vacuum, are: hydrogen 1.000263, oxygen 1.000507, nitrogen 1.000555, air 1.000540, and CO_2 1.000948. The values for N_2 were found to be independent of the frequency between 1230 and 600 meters, and to be proportional to the pressure from 44 to 69 cm. The values for air, N_2 and O_2 differ by 8 per cent from those of Boltzmann and of Rohmann.

THE initial object of the following investigation was to measure the magnetic susceptibility of oxygen. The general plan was to measure the change in frequency of an oscillating circuit when the pressure of the gas in the magnetic field of the circuit was changed. In the development of the method it was soon found that correction must be made for the distributed capacity of the coil used due to the change in the gaseous dielectric. The investigation was thus naturally turned first into determinations of the dielectric constants of gases as reported here, and the determination of the magnetic susceptibility of the gases is left for future investigation.

The method of determination of the change in frequency was based upon the heterodyne principle, which has been used for several years by Professor A. P. Carman and his students in this laboratory in measurement of dielectric constants.[1] There are two oscillating circuits, containing three-electrode valves. One circuit is used as a constant reference circuit. The second circuit contains air condensers, one of which can be altered in capacity by the change of the dielectric. The beat frequency between the two circuits gives a direct and exceedingly sensitive means of noting a change of frequency of the second circuit. The beat frequency can be adjusted in each case to that of a standard tuning fork by chang-

[1] W. H. Hyslop and A. P. Carman, Phys. Rev. **15**, 243, 1920; also theses and other unpublished MSS.

ing the capacity a known amount. Whiddington[2] used similar heterodyne circuits for the measurement of small displacements by measuring the change of capacity between two parallel plates when one plate was moved with respect to the other. Belz[3] has recently used Whiddington's method for the measurement of the magnetic susceptibility of certain salts.

The type of circuit used in the present investigation is shown at A and B in Fig. 1. The inductances L_a and L_b are wound in toroid form to eliminate stray fields. Two "Radiotron UV 202" power tubes are shown at PT_1 and PT_2. To prevent temperature variations about these tubes they were shielded with cardboard cases. The filament battery BA_1

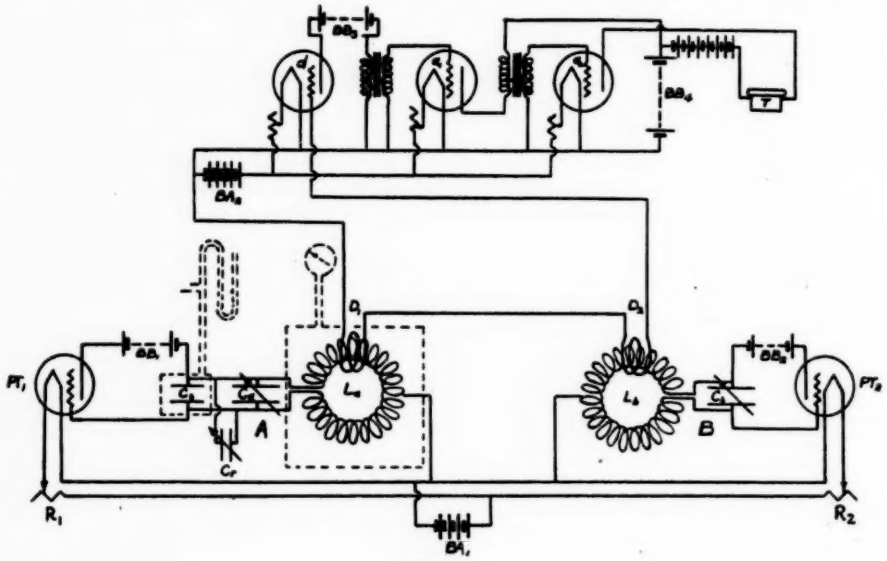

Fig. 1

consists of two sets of four storage cells in series connected in parallel, each cell having a capacity of 320 ampere hours. In the final experiments the resistances R_1 and R_2 were omitted, the e.m.f. of 8 volts at the battery being just sufficient to furnish the rated potential of 7.5 volts to the tubes. The plate batteries BB_1 and BB_2 are dry cell radio batteries each of 43 volts.

The beat frequency is produced by the use of two detector coils D_1 and D_2 which consist of five turns each wound loosely around L_a and L_b as shown. These coils are connected in series and to a detector and two stage amplifier, shown at the top of Fig. 1. The plate batteries BB_3 and

[2] R. Whiddington, Phil. Mag. 40, 634, Nov. 1920.
[3] U. M. Belz, Phil. Mag. 44, 479, 1922

BB_4 consist of 20 storage cells of small capacity giving an e.m.f. of 40 volts. As shown, an additional battery of this type is put into the plate circuit of the last amplifier. The output of the amplifier is connected to a Baldwin receiver T.

This method of producing the beat frequency between the two circuits eliminates the variations in the frequency of circuits A and B due to variations in the detector system and makes possible the operation of the system at a distance so that no variations are produced by the movements of the operator. The circuits A and B were enclosed in a

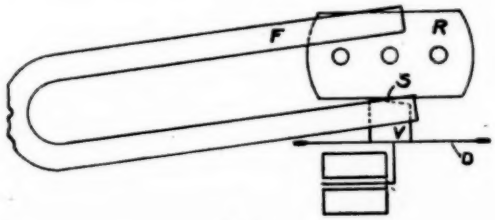

Fig. 2

wire cage supported on strong wall brackets and were sufficiently separated so that there was practically no coupling between the two circuits. It was found that the smaller the dimensions of the batteries BB_1 and BB_2 the less was the change of frequency due to a change in the position of external objects. In the experiments no trouble of this sort was appreciable but as a safeguard the compact radio dry batteries were used because of their size.

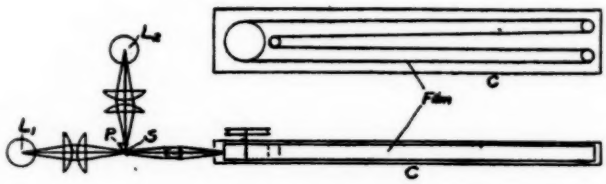

Fig. 3

A detail of the mounting of receiver T is shown in Fig. 2. The diaphragm D carries a light vane V which forms with the razor blade R a wedge shaped slit S. A tuning fork F forms a similar wedge at the other end of the slit. Thus the vane, the tuning fork and the razor blade form the sides of a triangular slit S, the razor blade forming the upper side. S is strongly illuminated by the system shown in Fig. 3, the low voltage concentrated filament lights L_1 and L_2 each illuminating half of it.

From the condensing lenses the light from L_1 passes directly to the slit S while that from L_2 is reflected upon the slit by a right angle prism P. The camera is a box about 4 ft long and 8 by 3 inches in cross-section. It contains adjustable rollers so that a continuous moving picture film about three feet or more long can be mounted in it. The slit is placed with its length at right angles to the direction of motion of this film and an image of the slit is focused on the film by a lens as shown. To enable the operator to limit the exposure to the length of the film a shutter (not shown in the diagram) was placed immediately in front of the camera. The camera was driven by a spring motor of very constant speed. As the tuning fork and diaphragm vibrate, the slit is periodically altered in length and the resulting exposure is shown in Fig. 4 which is a print taken from a portion of one film. The six white portions of Fig. 4 indicate portions of six exposures produced on the film. In each exposure the

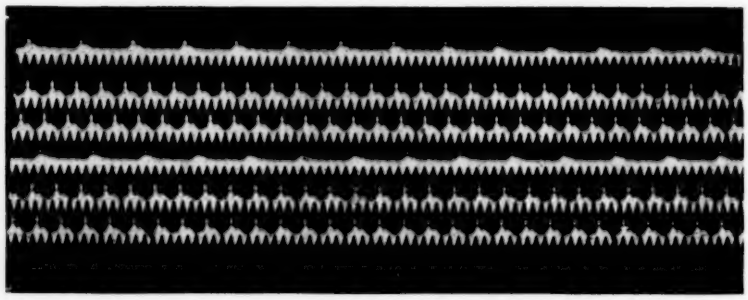

Fig. 4

record of the tuning fork is that with the finer teeth shown at the bottom of the exposure. The record of the vibrations of the diaphragm is at the top of the exposure. The record of the tuning fork is used as a measure of time in the determination of the frequency of the vibrating diaphragm as will be explained later. The frequency of the diaphragm thus recorded is the beat frequency between circuits A and B. If the frequency of circuit B is kept at a constant value then any change in the frequency of circuit A is equal to the change in the beat frequency which after being recorded can be measured against the tuning fork frequency.

The condenser C_1 was used in three different forms, the first of which is shown in Fig. 5. Six coaxial cylinders form the plates. Each end of each cylinder is cut away to a depth of one quarter of one inch along two opposite quadrants. Two brass plates were made and concentric grooves cut in them to fit the cylinders. These plates were then cut into quadrants A and B and the condenser was assembled and soldered together.

Alternate cylinders were soldered into alternate quadrants; the bottom quadrants were secured by screws, one of which is shown at D, to hard rubber quadrants and these quadrants were secured by screws, one of which is shown at E, to a marble base. This construction was adopted to give a rigid condenser in which there was little solid dielectric in

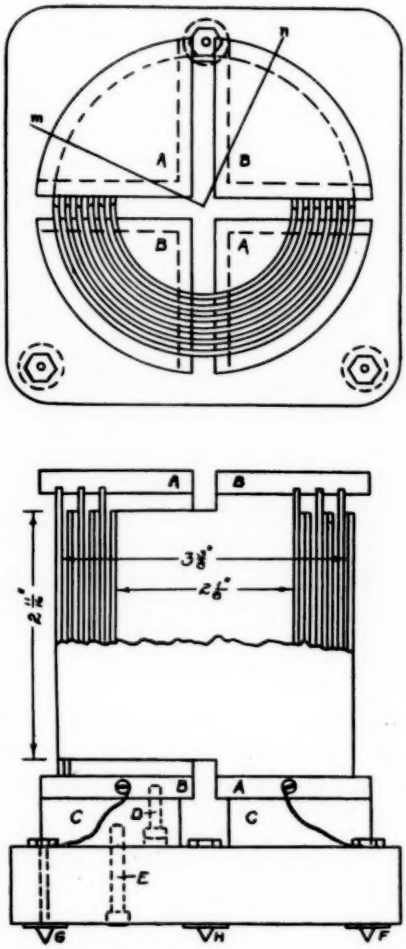

Fig. 5

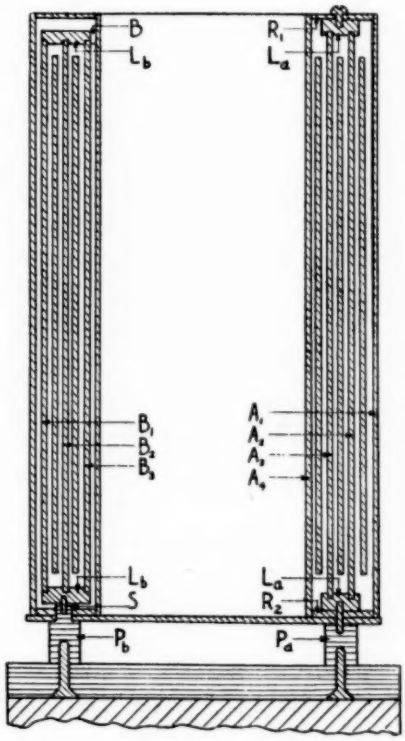

Fig. 6

the field. The condenser was carried on three points F, G, and H, and connections were made through the points F and G.

The second and third forms of the condenser C_1 will be denoted by C_2 and C_3, respectively. The results to be given later seem to indicate that the measurement with C_1 was subject to a small error due to a stray field between the bottom quadrants through the hard rubber and the

marble. For this reason C_1 was modified into the form C_2 and a new and larger condenser C_3 was made, so as to eliminate this error. A section through C_2 along the line mn (Fig. 5) is shown in Fig. 6. In this form the quadrants are mounted on hard rubber posts P_a and P_b which carry also, below the quadrants, a brass plate C connected to the lower quadrants B (Fig. 5). The quadrants A are insulated from the first set by shoulders S turned on the posts P_2. Small screws are used to secure the quadrants to the posts. Around the whole is placed a metal cap D also connected to the quadrants. In this way the whole field is confined within the condenser and only the small portion of solid dielectric at S and B is in the field. The third condenser C_3 was very similar to C_2 but with larger capacity.

These condensers C_1, C_2 or C_3, were enclosed in a glass bell jar and arranged so that the identical placing of the condenser could be secured. In the base of the bell jar was placed a junction of a thermocouple and a gas outlet.

Capacity C_a (Fig. 1) was a high grade circular-plate variable condenser constructed of cast brass plates. By several calibrations the relation between the reading in degrees and the capacity of such condensers has been shown to be strictly linear over the greater part of the scale. Capacity C_b (Fig. 1) was identical with C_a and C_r was similar to C_a, differing only in size. C_r was fitted with a slow motion screw. A mirror was attached and small angular displacements were measured by a telescope and scale.

C_r and C_1 were calibrated in terms of degrees along the straight line portion for C_a. For purposes of calibration C_1 and C_a are both connected as indicated by A (Fig. 1), C_a being set near the lower end of its linear calibration. Circuit B was then adjusted to the same frequency as circuit A by finding the point of zero beats between the two circuits. This method of adjustment was extremely accurate since the beats could be decreased to the point where they could be easily counted audibly before they died out, a fact probably due to the coupling between the circuits being so small that there was little tendency for the circuits to be forced into the same frequency by their mutual inductance. After this adjustment of circuit B, condenser C_1 was disconnected by removing the leads in the base of C_1 from the quadrants and C_a was readjusted until the circuits were again at the same frequency. In this manner only that portion of C_1 was removed from the circuit in which the dielectric was changed. The difference between the two capacities of C_a was then the capacity of C_1. The difference between the capacities of C_r when set at two points along its straight line calibration, was determined in

the same way and the value of C_r per degree and in terms of degrees on C_a found. After these calibrations C_a was removed from the circuit.

C_2 was measured in the same way as C_1. In the case of C_3 the capacity was too large to permit direct substitution along the straight line portion for C_a and the calibration was carried out in the following manner. C_3 was connected in the circuit A and C_a set near the lower end of its linear calibration as before and the circuit B was brought to the same frequency. Then C_3 was disconnected and C_2 connected into the circuit. C_a was then re-adjusted as before until the circuits were at the same frequency. The capacity change in C_a was then equal to the difference between C_3 and C_2, and C_3 was taken as the sum of this value and C_2.

These capacity measurements were checked by a capacity bridge method and the values agreed within about 1 per cent.

The bell jar containing the condenser C_1 was connected through the gas outlet to a system of stop cocks leading to an oil pump and a gas reservoir. Commercial gases were used, supplied in the usual high pressure cylinders. The reservoir was constructed from a two foot length of four inch steam pipe fitted with caps on each end. The gases were passed through a calcium chloride tube about three feet long into the reservoir until the pressure was sufficient to produce, after expansion into the evacuated bell jar, a final pressure equal to that of the atmosphere. Pressures were read on an open manometer M. The temperature was determined by the thermocouple and a potentiometer. The temperature was always found to be equal to that of the room except for a small momentary change after expansion.

The procedure in the experiment was as follows. The pressure in the bell jar was reduced to less than 1 mm as measured on a small closed manometer in J and the frequency of the circuit B was adjusted to a value about 100 cycles greater than that of circuit A. After closing the stop cock and stopping the motor used to drive the pump, a record n_1 was made of the beat frequency. By opening the second stop cock the gas was allowed to expand into the bell jar and a second record n_2 was made. C_r (Fig. 1) was then decreased by about one or two degrees and a third record n_3 was made. The total time for making the three exposures was about twenty five seconds. The initial and final readings of the telescope, d_1 and d_2 and the difference from atmospheric pressure were noted. The temperature was measured and the barometric pressure read.

The film on which the records were made was driven at a very constant speed. This made possible a very easy method of counting the beat frequencies n_1, n_2, and n_3. Twenty five cycles on the tuning fork record

were counted and a pair of dividers set to this measure. The dividers were then used to lay off four hundred cycles by intervals of twenty-five, beginning at a point where a peak on the tuning fork record was coincident with a peak on the beat record. The number of beat cycles in this length were then counted in a similar manner, estimating to one tenth of a cycle. By keeping the beat frequency small this method was very accurate and by checking from time to time the method of counting was found to be exact.

In the equation

$$dn/dC = n/2C \tag{1}$$

dn is proportional to dC if n and C are not appreciably altered.

The change of capacity due to the change of dielectric from a vacuum to a gas is equal to $(K-1)\ C_1$ where K is the dielectric constant of the gas. Due to the change in capacity by the introduction of the gas we have the change of frequency n_g equal to n_2-n_1, and due to the change in capacity in C_r we have the change n_c equal to n_2+n_3, since the beat frequency was carried through zero to a value in the opposite direction. This method was adopted in the change of C_r to produce a change which could be accurately measured while keeping the beat frequency down to a value which could be easily counted.

By equation (1) we have

$$(K-1)C_1/C_r = n_g/n_c \tag{2}$$

where K is the dielectric constant of the gas at the temperature and pressure of the experiment. The dielectric constant of a gas, as will be seen by results to be given later, is directly proportional to the pressure. Assuming that the temperature effect is only one of density we may, therefore, reduce K to its value at one atmosphere and zero degrees by dividing the right hand member of Eq. (2) by P_0 where

$$P_0 = (273/T)\ (P/76) \tag{3}$$

P being the pressure in cm of mercury and T the absolute temperature of the gas. The value of C_r in Eq. (2) was determined by the equation

$$\Delta C_r = (d_1-d_2)\ 180R/2\pi D \tag{4}$$

where R is the value of C_r per degree in degrees on C_a, and D the distance between the telescope and scale. For convenience in calculating, Eq. (2) was used in the form

$$\frac{(K-1)\ C_1}{\Delta C_r'} = \frac{\Delta n_g}{\Delta n_c/(d_1-d_2)} \tag{5}$$

where

$$\Delta C_r' = \Delta C_r/(d_1-d_2)$$

or the change of the capacity of C_r per cm deflection in the telescope. It was further assumed that variations in the values of $\Delta' n_c$ throughout the experiments in which circuit A was unaltered were experimental rather than variations in the circuit itself and the mean of all such values was used in each calculation. Since in Eq. (2) Δn_g and Δn_c appear only in the ratio between the two quantities it is immaterial whether these quantities are expressed in cycles per second or involve some other unit of time. The tuning fork had a frequency of 512 cycles per second. It was found much more convenient to count the records by hundreds and therefore all values given for the changes in frequency in the following data are per 400 cycles of the tuning fork rather than per 512. The final equation for determining the dielectric constant is

$$K=1+\frac{\Delta n_g\times 180\times 76\times RT}{2\pi D\times 273P\times[\Delta n_c/(d_1-d_2)]\,C_1}. \tag{6}$$

The following precautions were followed in the experimental work.

1. Considerable trouble was experienced due to changes in the filament temperatures of the oscillating tubes. This trouble was removed by eliminating as far as possible, all contacts in the filament circuits and soldering as many of those which remained as was convenient. It was for this reason that resistances R_1 and R_2 (Fig. 1) were removed.

2. Variations probably due to (1) were originally ascribed to the plate batteries. Although such variations probably did not originate in the plate batteries, yet the size of these batteries determined quite largely the magnitude of the variations. When, for instance, small storage batteries were replaced by the equivalent number of dry cells, which occupied much more room, the variations in frequency were increased several fold. For this reason the radio batteries referred to above were used. It was also found better to keep these batteries at some distance from the wire net by which the system was shielded.

3. The variable condensers C_a and C_r were first equipped with flexible cables connecting the rotating plates with the binding posts. Using them in this form seemed to give slight variations in the measurement of the capacities C_1 and C_r but after rigid sliding contacts were substituted for the cables such measurements could be repeated as closely as C_a could be read.

4. The insulating property of each of the condensers C_1, C_2, and C_3, was tested by charging and connecting with an electroscope and noting the rate of discharge. It was found that no noticeable collapsing of the leaves occurred during five minutes.

5. No noticeable advantage was gained by shielding the oscillating circuits but this precaution was carefully followed. The detector system

was not shielded but no trouble was experienced in using it in this manner. This system was placed several feet from the cage containing the oscillating circuits.

6. Upon request the manufacturers furnished a statement in which a purity of 99 per cent was claimed for the nitrogen, oxygen and hydrogen used. The carbon dioxide was obtained in the commercial cylinders and was carefully dried. The air was taken from the air mains and carefully dried.

7. Before any experiments were performed time was allowed for the tubes to come to a uniform temperature. All doors and windows to the room were kept closed so that no air currents were present.

8. The motor driving the air pump was stopped before each experiment.

9. Experiments were performed to test for changes in frequency due to changes in the bell jar system or due to any drift in the beat frequency. These experiments showed such variations to be not greater than 0.2 of a cycle per 400 cycles of the tuning fork.

10. In changing from one gas to another the reservoir and drying tube were pumped out to about 2 mm pressure, filled to atmospheric pressure with the new gas then again pumped out and refilled before any data were taken.

Experimental Results

Table I gives a set of readings in detail so as to show the character of the measurements.

TABLE I

Run No. 1, Nitrogen

$C_1 = 77.5°$ on C_a; Total cap. = 675 m.m.f. (approx.); $D = 268.6$ cm; $\lambda = 393$ meters.

P	T	Δn_g	$\Delta n_c/(d_1 - d_2)$	K at 1 atm. and 0°C
		C_r set at 130°		
74.9	296°K	99.0	52.1	1.000551
74.9		99.0	51.8	1.000551
74.9		100.2	53.2	1.000556
74.7		96.5	51.4	1.000538
74.7		96.5	51.4	1.000538
74.57		97.5	51.9	1.000545
74.57		98.0	51.6	1.000547
		Means:	52.0	1.000547
		C_r set at 135°		
75.8	296	97.2	51.35	1.000537
74.5		95.5	52.3	1.000537
75.0		99.0	51.6	1.000553
74.6		97.9	51.7	1.000550
		Means:	51.74	1.000554
		C_r set at 150°		
75.1	296	93.8	48.7	1.000554
			Grand mean:	1.000546

TABLE II

Summary of all sets of readings

Number of run	Gas	No. of readings	Pressure mean	Wave-length λ in meters	K reduced to 0°C and 1 atm.
1	N_2	12	74.9 cm Hg	393	$(C_1)(1.000546 \pm .0^{5}62)$
3	N_2	15	74.3	593	$1.000555 \pm .0^{5}20$
4	N_2	9	74.2	1230	$1.000556 \pm .0^{5}25$
5	N_2	1	75.65	593	1.000558
	N_2	1	62.5	593	1.000558
	N_2	1	48.2	593	1.000557
2	O_2	5	74.8	393	$(C_1)(1.000490 \pm .0^{5}54)$
6	O_2	7	75.0	593	$1.000505 \pm .0^{5}26$
7	O_2	1	74.2	593	1.0005111
	O_2	1	48.4	593	1.000512
	O_2	1	33.7	593	1.000512
8	H_2	5	74.7	605	$1.000263 \pm .0^{5}15$
9	CO_2	7	73.0	605	$1.000948 \pm .0^{5}16$
10	Air	6	75.0	605	$1.000540 \pm .0^{5}11$

Runs No. 1 and 2 were made using C_1, and are given merely for comparison with the later data. It will be seen that the later runs made using C_2 and C_3 give values about two per cent higher than were obtained in Runs 1 and 2. This difference is ascribed to the stray field through the hard rubber and marble base of C_1 in which the dielectric was not changed and for this reason the values obtained in runs 1 and 2 are not included as a part of the final values. It was also found that the values obtained in the later runs check among themselves more closely than do the values from runs 1 and 2. The mean deviations from the mean for each run is given in the last column and is seen to be much greater for runs 1 and 2.

In run 3 data were taken with both condensers C_2 and C_3. Where C_2 was substituted for C_3 a sufficient portion of C_a was added to the circuit to bring the frequency to the same value as when C_3 was used. The means of 11 readings with C_3 and of 4 readings with C_2 check exactly. This fact is conclusive evidence that the values are independent of the condenser, and since the solid dielectric in the case of condenser C_2 contains perhaps three times as great a part of the total capacity of the condenser as in the case of C_3, it is also evident that no appreciable error is introduced by this solid dielectric. Run 4 was made under the same conditions as run 3 except that the wave-length was changed by increasing the number of turns on the coils L_a and L_b (Fig. 1). It is seen that the same values are obtained at this wave-length as are obtained at approximately one half the wave length; it is therefore evident that there is no variation of the dielectric constant with frequency over this range. It is perhaps well also to mention here that in these experiments the changes in frequency were so small that it was found advantageous to take all beat frequency records on the same side of the point of reson-

ance. This is also a check on the general method used where in changing C_r the beat frequency was carried through its zero value to a point on the opposite side. Runs 5 and 7 show that the dielectric constant is strictly proportional to the pressure for pressures less than one atmosphere.

In considering the absolute values in relation to the values given by previous investigators the following facts are to be noted.

1. The values of Boltzmann for carbon dioxide and hydrogen are checked to less than one half of one per cent.

2. The values for nitrogen, oxygen and air are lower than the values of Boltzmann and Rohmann with the ratios given in Table III.

TABLE III

Values of $K-1$

Gas	Boltzmann (I)	Rohmann (II)	Fritts (III)	Ratio (II/III)
Air	.000590	.000580*	.000540	1.074
CO_2	.000946	.000989	.000948	1.04
N_2	———	.000606	.000555	1.090
O_2	———	.000547	.000507	1.08
H_2	.000264	.000282	.000263	1.072

Since the ratios in Table III are all near the same value and the values of Boltzmann for carbon dioxide and hydrogen are checked so closely the present results seem to indicate that the value for air of 1.000580 which has been assumed by Rohmann should be replaced by 1.000540.

Errors. Of the quantities involved in the Eq. (6) R, C_1, C_2 and C_3, and D were measured and checked with a high accuracy. The temperature was measured to one degree and is therefore subject to a maximum error of about 0.3 of one per cent. The pressure P was measured to one mm of Hg and is subject to a maximum error of about 0.13 per cent. The values of d_1-d_2 are subject to an error not greater than 0.2 of one per cent. The errors in n_g and n_c are of the same order as the above errors.

In conclusion, the author wishes to thank Dr. Jakob Kunz under whose direction the investigation was carried out. The author is also grateful to Professor A. P. Carman for the helpful suggestions which he has made with regard to the work.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
February, 1923.[4]

* In order to check the values of Klemençiç more closely this value for air was assumed by Rohmann.

[4] Received September 22, 1923—Ed.

ELECTRICAL RESISTANCE AND THERMO-ELECTRIC POWER OF THE ALKALI METALS[1]

By Charles C. Bidwell

Abstract

Electrical resistance and thermo-electric power of the five alkali metals, −183°C to 250°C.—Pure samples of the metals were fused into glass or quartz tubes, and measurements were made by means of thermo-junctions sealed into each end. Enough points were secured in each case to determine the slopes and the breaks in the curves. In both the resistance and thermo-electric power lines, changes of slope are observed beginning gradually 100 degrees or more below the melting point. These are taken to indicate *transformations* in each case from an α to a β form. These transformations occur at approximately the temperatures, 50°C for Li, −20°C to +20°C for Na, −120°C for K, −35°C for Rb, and −80°C for Cs. In all cases a sharp rise in thermo-electric power and resistance occurs as the melting point is approached. The *temperature coefficients* of resistance decrease smoothly with increasing atomic weight for all forms.

Atomic heat of electrons in the alkali metals.—The atomic heat of electricity as computed from thermo-electric data is approximately 0.24 cal. for Na and K, and 0.58 cal. for Rb and Cs. The values are too small to account for the observed excess of the atomic heats for these metals above the equipartition value.

Introduction

BEFORE any theory of electrical conduction can be regarded as being most consistent with the facts or as most clearly explaining observed behavior, more complete knowledge of the actual behavior of pure materials should be at hand. It has seemed to the writer that our knowledge of the experimental facts of electrical conduction is very meager. Our knowledge of the change of electrical resistance with temperature is quite fragmentary. With the so-called metallic conductors we have a positive temperature coefficient, and with the non-metallic conductors a negative coefficient. With certain intermediate elements (metalloids) the coefficient is positive or negative depending upon the temperature. A search of the literature reveals the fact that only in a few isolated cases have sufficient data been taken on pure materials over wide temperature ranges to warrant positive statement of the resistance law. The observations at the Leiden laboratory have given us for a number of metals most accurate and extended data over the low temperature

[1] The investigation upon which this article is based was supported by grants from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

range but there is need of data on many more metals and non-metals widely distributed over the Periodic Table.

In the present studies on the alkali metals[2] measurements of thermo-electric power were made through certain temperature ranges simultaneously with the resistance measurements, or as nearly simultaneously as was consistent with the requirement of a uniform temperature over the specimen for the resistance measurement and the establishment of a temperature gradient for the thermo-electric power reading. There is considerable evidence that the relation between thermo-electric power and temperature for a pure material in a given crystalline modification is expressed by a straight line and that a change of slope occurs only when the material undergoes a transformation. If this may be assumed, the thermo-electric power line gives a means of detecting changes in crystalline structure. The present work is the first contribution in a systematic study of the resistance temperature relation for pure elements, the plan being to study the elements group by group throughout the Periodic Table. Resistance curves for the five alkali metals on specimens of very high purity together with the thermo-electric power lines have been obtained. The measurements were carried from liquid air temperatures over a range of 400° or more, in all cases through change of state, with observations on the liquid state.

Methods Employed in the Present Work

It was the aim of the writer to secure resistance measurements at temperatures sufficiently close together to establish definitely the resistance-temperature relation, and to secure thermo-electric power data on the same specimen simultaneously, so that collateral information might be at hand of possible transformations which might account for peculiar behavior of the resistance lines.

Because of the great chemical activity of these metals, special technique is required in their manipulation. Caesium, rubidium, and lithium were reduced by the writer from c.p. chlorides specially prepared by Dr. J. Papish of the Chemistry Department, Cornell University. Spectroscopic tests of both the salts and the metals were also made by him. Except in the case of lithium the metals were run into lead glass capillary tubes through the walls of which were fused two pairs of fine platinum wires about two inches apart. In the case of caesium and rubidium, the tubes were sealed off in vacuo; potassium and sodium were handled under "nujol," a mineral oil mentioned by Bridgman as especially good for this purpose. One wire of each pair was cut off close to the glass and

[2] A summary of previous work on the alkali metals is given at the end of this paper.

a constantan wire soldered to it. The arrangement is shown in Fig. 1. The platinum and constantan wires of each junction were of sufficient length to extend to a Dewar cylinder where they were connected to copper leads. The contacts with the copper wires were kept at the temperature of melting ice. The platinum-constantan contacts were made through the metal inside the capillary tubing. Temperatures at the two points in the metal could be determined by connecting the junctions in turn to the potentiometer.

The platinum-constantan junction was adopted after considerable experimentation as especially suitable for the low temperature range (0° to −180°), where the platinum-platinrhodium junction is inoperative. Platinum-constantan was found at least as reliable as iron-constantan and eliminated a soldered joint on one of the wires of each pair. To

Fig. 1

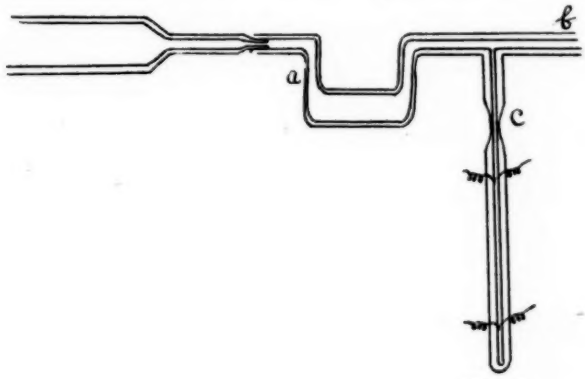

Fig. 2

measure resistance, current was sent in from a storage battery by way of the constantan wires and the fall of potential measured by means of the platinum leads. Before and after such readings temperatures were checked at the two junctions.

The current was measured by determining the fall in potential across a standard Hartmann and Braun resistance in series, whose value was either 0.01 or 0.001 ohms. For thermo-electric measurements a temperature gradient was established along the specimen, the temperatures measured at each end, and the electromotive force between the platinum leads determined. A temperature difference of from six to ten degrees was found most suitable for accurate work. The value of this difference could be determined to within 0.05°, whereas the actual temperature at either end was not known better than about ±0.5°. Potentiometer readings were good for three decimal places in temperature, which was beyond the accuracy of the calibration. Our knowledge of the

fixed points and the need of interpolating between such points necessitated discarding two of the potentiometer figures as not significant as regards actual temperature, but the decimal places are significant in taking the difference between two temperatures close together. The difference as given by the potentiometer, divided by the slope of the calibration curve at the point, i.e., by the thermo-electric power of the platinum-constantan junction at the temperature in question, gives the temperature difference with very high accuracy, at least that indicated above. The thermo-electric power as thus computed was plotted against the mean of the temperatures of the two junctions. The potentiometer used throughout was an Otto Wolff low resistance instrument.

For the calibration of the platinum-constantan couple, liquid air that had been boiled violently for several minutes was taken as giving the boiling point of liquid oxygen, viz., −183°C, carbon dioxide snow and ether as −78°C, mercury freezing point as −40°C, and fairly good points supported by readings of a Reichsanstalt pentane thermometer, viz., the melting point of ether −117°C, of acetone −94.6°C, and of chloroform −65°C. The gap between −117° and −183° is covered by interpolation based upon the constants of the equation for the junction as determined from the known points. Above the ice temperature there are numerous good fixed points.

Temperature Bath and Control

The capillary tube containing the metal was placed in an outer protecting glass tube. This was encased in a heavy brass tube whose walls were about ¼ inch thick. Resistance measurements were first made at the temperature of melting ice. These readings were repeated as a check before and after every "run" or set of observations. The specimen with the leads emerging from the top of the brass tube was packed in wool and lowered into a large Dewar cylinder where it was completely immersed in liquid air. Resistance measurements were taken at this temperature and then the specimen was raised in the flask until it was entirely above the surface of the liquid. The space around the specimen and above it for about six inches was packed tightly with wool. Through this packing a glass tube extended to the bottom of the cylinder. Liquid air was sprayed through the wool from above until both junctions were steady at −183°C. The specimen thus packed was then allowed to stand, whereupon its temperature slowly rose, that of the upper junction slowly drawing away from that of the lower and slowly increasing the temperature gradient along the specimen. If the difference became greater than twelve or fifteen degrees, air was blown through the glass

tube, thus forcing the cold air from the bottom up through the wool, lowering of course the temperature of the specimen as a whole but also reducing the temperature difference. It was found that by continuing this stream of air up from the bottom, the two junctions could be brought to the same temperature reading. If the air stream were continued until no liquid air remained and then was cut down to a very slow current the temperature of the two junctions could be maintained alike as the specimen slowly heated to room temperature. On some runs four hours or more were required for the rise from $-183°$ to $0°$. By cutting down the air stream or shutting it off a temperature difference would develop and this difference could be quite satisfactorily controlled by the air stream. Many of the resistance measurements were made with the temperature difference reduced to zero but probably a majority were taken when still three or four degrees difference existed over the length of the specimen. The value obtained was plotted against the mean. Such values were found to fit the curve and to duplicate points obtained with the greater time and trouble required for uniform temperature. Thermo-electric power readings were taken with any temperature difference between $2°$ and $20°$ or more (in some cases). Since temperatures were slowly changing, readings were taken in the order, e.m.f. across specimen, top junction, bottom junction, top junction, e.m.f. across specimen. The change in the two readings for the top junction was usually of the order of a few tenths of a degree and the average was taken. Usually the initial and final e.m.f. readings were unchanged. The heavy tube served to equalize the temperatures and apparently to produce a uniform gradient along the specimen. Without the brass casing the gradient rapidly became large and the data when plotted proved to be quite erratic. The brass tube made the difference between success and failure in getting consistent, reproducible thermo-electric power data.

For temperatures above room temperature, the Dewar was replaced by a tubular, spirally-wound, electric furnace. The temperature gradient was controlled by raising or lowering in the furnace. The resistance measurements were checked by observations in constant temperature baths of boiling ether, chloroform, alcohol, water and anilin.

Caesium

This metal was prepared by heating the c.p. chloride with pure metallic calcium in vacuo, the charge being placed in a long pyrex tube. On heating to about 400°C the reaction sets in, causing a glow to extend throughout the mass with condensation of caesium metal in the cooler

part of the tube. This was driven along the tube, redistilling at temperatures much lower than that of the reaction, the redistillations serving to purify the metal. The pyrex tube was finally sealed off separating the metal from the non-volatile materials in the hot end of the tube but still leaving it connected to the pump. To the pyrex tube was connected by means of thick-walled rubber tubing a lead glass tube containing an enlargement for receiving the metal. Between the enlargement and the pump was connected the glass capillary containing the platinum leads. The arrangement is shown in Fig. 2. The capillary and chamber were next well heated with a Bunsen flame while further exhaustion was carried on. The tube was then sealed off at *b* and the molten metal allowed to run into the lead glass chamber from the pyrex tube and the tube sealed off at *a*. The metal was then allowed to run into the capillary. The tube was filled very nicely on the first trial, as shown by good contacts at all leads. The capillary was finally sealed off at *c*, leaving space above the metal for expansion. The metal remaining in the enlargement was used for determination of melting point and for spectroscopic tests of purity. The tests indicated a trace of sodium as the only impurity. The melting point was found by immersing in water whose temperature was varied until the metal on agitation showed pasty condition. The average of many determinations which agreed closely was 27.4°C. Melting points for caesium tabulated in Landolt-Börnstein vary from 25.30 to 28.2°, the latter being the latest and presumably the most accurate value.

Resistance measurements at 0°C gave initially 0.01538 ohms. After immersing in liquid air and taking a number of preliminary observations at low temperatures the 0° reading was found to be 0.01530. Two sets of observations were then made over the range from 0° to −192°, giving the data shown graphically in Fig. 3. The resistance at 0°C after these runs was still 0.01530. After standing for two days the resistance at 0°C was found to be 0.01500. Observations were then made on the molten metal. After heating to 97°C and back, the 0°C reading was found to be 0.01503. Two sets of observations were then made in the range 0°C to 98°C. Above 98°C the specimen became blackened through reaction with the lead glass tube. Thermo-electric power measurements were made during these runs in the manner already indicated. The results are also shown in Fig. 3. The break in the thermo-electric power line at −80°C indicates presumably a molecular rearrangement or modification of some sort. The graph shows the ratio of the resistance at any temperature to that at zero. Specific resistance was not determined. The resistance relation is linear between −190°C and −80°C.

Between −80°C and 0°C a marked curvature indicates a different law. The resistance points by themselves do not conclusively bring out the change at −80°C but in connection with the thermo-electric power line the meaning of the deviation of the resistance points from the straight line followed up to −80°C is apparent. Above 0°C the metal apparently shows evidence of the approaching fusion. This behavior on approaching the melting point is characteristic of all the alkali metals as will be noted in the other curves. It suggests a gradual loosening up of the crystalline structure, the lattice however holding together and retaining the metal in the solid state until the complete collapse at the

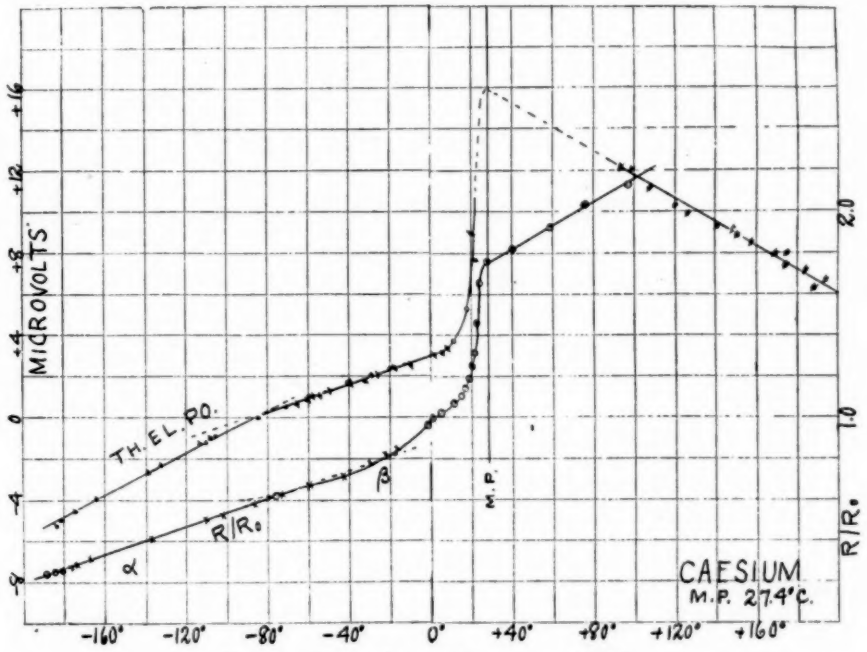

Fig. 3. Curves for caesium, m. p. 27.4°C.

melting point. The very great increase in thermo-electric power and resistance occur while the metal is solid. A very careful study of a sample of the metal in the evacuated tube showed the solid state with no evidence of pasty condition until at least 27.0°C was reached, whereas the changes in thermo-electric power and resistance are noticeable as far back as +12°C. On cooling there is no such gradual change on approach to the melting point. The change sets in abruptly, the decrease in thermo-electric power and resistance being extremely sharp at first, although the final condition is apparently not reached for fifteen degrees or more below the melting point. The exceptional purity of all of these metals,

as indicated both by spectroscopic tests and by the melting points, makes it rather unlikely that the gradual changes on approach to the melting point from below are due to impurity. The freezing point in all cases was sharp but the loosening up of the lattice in the solid seems to start many degrees below the melting point. A number of cooling curves were taken on potassium. The change was absolutely abrupt at 62.5°. It is regretted that slow heating curves were not taken on some of these metals to test the abruptness of the melting. Bridgman is positive that premature rounding of the melting curve is an indication of impurity. A further investigation of this point is planned. It should be pointed out however that the curves shown are not melting curves and that the material is not in an unstable condition in this region where the lines are curving. The existence of two modifications, an α form, stable at low temperatures, and a β form, at higher temperatures, seems to be characteristic of the whole alkali group as will be noted from the curves.[3]

For molten caesium, the thermo-electric power and resistance lines were perfectly straight. The initial resistance run to 98°C gave a somewhat greater slope (temperature coefficient) than a run after observations on thermo-electric power to +200°C had been carried out. Resistance measurements made on the slow cooling from 200°C gave a straight line with slightly less slope. As the specimen had become completely blackened through reaction with the lead glass, the initial readings to 98°C were taken as giving the better value of the temperature coefficient. The temperature coefficient was changed by this slight contamination from 0.00260 to 0.00240.

Rubidium

The rubidium was reduced from the chloride with calcium in vacuo and the same procedure followed as with caesium. Several attempts were necessary before the metal was finally obtained in the capillary with good contacts at the leads. The material used in the first trials had to be worked over and in this process suffered contamination, for the specimen as finally successfully mounted was found on later spectroscopic tests to

[3] Note added February 1, 1924.—X-ray diffraction patterns recently obtained by the writer on lithium at various temperatures show a gradual fading out or obliteration of the lattice structure above the transformation temperature here reported, the β form therefore being the amorphous form. This is in agreement with the previously known fact that sodium is nearly amorphous (shows little or no x-ray diffraction pattern) at room temperature but is a body-centered cube at liquid air temperature, also with the fact that potassium shows no pattern at room temperature, while a clear pattern, body-centered cube, is obtained at liquid air temperature (Hull, Phys. Rev. **10**, 661, 1917; McKeehan, Proc. Nat. Acad. Sci. **8**, 8, 1922).

have considerable impurity of potassium. The melting point of this sample was found to be only 33.0°C. Thermo-electric power and resistance of this specimen, rubidium (1), are shown in Fig. 4. A second sample, rubidium (2) was spectroscopically pure and its melting point satisfactory, 37.2°C. Thermo-electric power and resistance are shown for this specimen, Fig. 5. The melting points, as reported by Landolt-Börnstein, for rubidium are 37.8°C (Eckard 1900) and 38.5°C. (Erdmann and Köthner 1896). The specimen, rubidium (2), was lost on the first attempted run through the melting point, the expansion cracking the glass tube. Since there was such a fair general agreement between

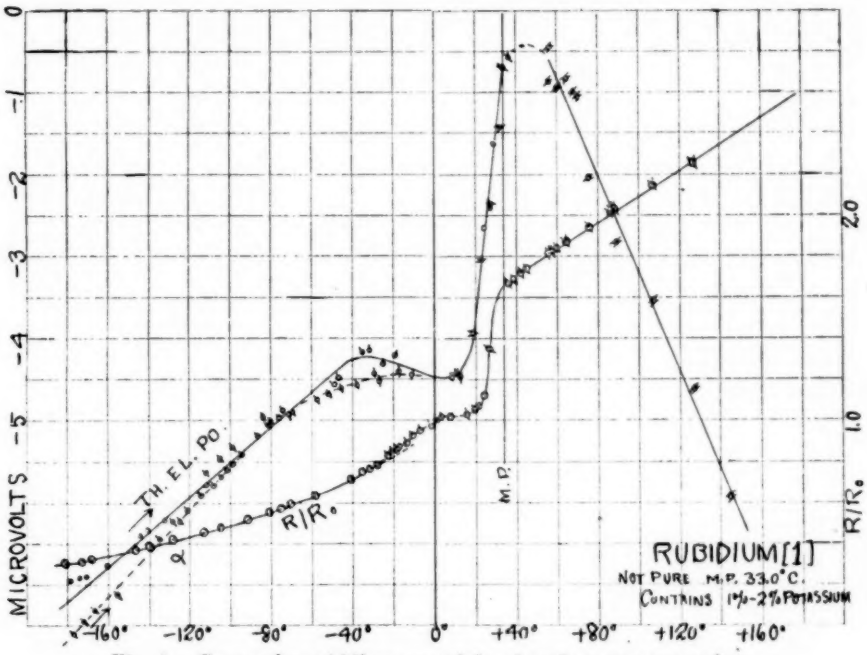

Fig. 4. Curves for rubidium containing 1 to 2 percent potassium.

the curves for the impure specimen and those for the better one and since data were obtained on the impure specimen through fusion and on the liquid metal as far as 150°C, a further attempt to check up the data on the liquid metal with a purer specimen was not made. The metal was found to possess α and β modifications, the transformation occurring at about -30°C.

The behavior on approach to the melting point is similar to that of caesium. The change in the resistance reading at 0°C for specimen (1) after cooling to liquid air temperature was 0.8 per cent. After melting and heating to 75°C and again cooling the resistance at $+20$°C had changed

from 0.0146 to 0.0156 ohms. Due to the formation of cavities on freezing it is not to be expected that the values of the resistance in the solid state will be repeated after melting. If the value at 0°C is redetermined however, the values of R/R_0 should repeat. This they did satisfactorily. The value selected for R_0 for the ratio R/R_0 for the liquid state was the lowest observed value, the value in which the effect of cavities on the mean cross-section was least. This value effects only the computation of the resistance change on melting and does not enter into the computation of the temperature coefficient. With specimen (2) the change in

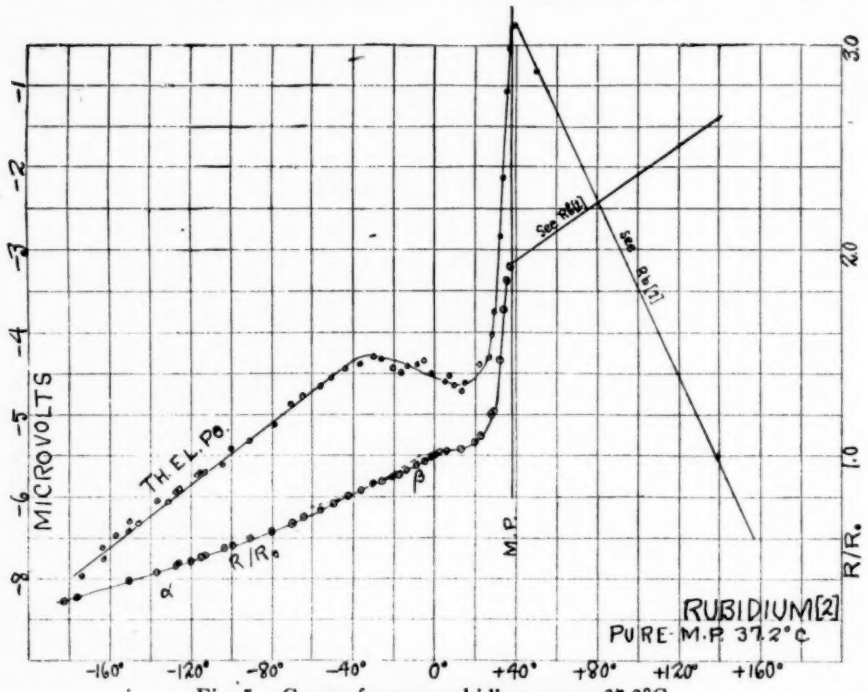

Fig. 5. Curves for pure rubidium, m. p. 37.2°C.

the value at 0°C after taking the low temperature readings was about two per cent. The mean value of R_0 was used for the ratio R/R_0.

In plotting all curves large circles were used for resistance and small circles for thermo-electric power. Circles without tails indicate the first run. Circles with one tail, the second run; two tails, the third run, etc. The extent to which the various runs repeat can thus be noted.

Potassium

The potassium metal was from old stock. The source was not known. Spectroscopic tests indicated high purity, the only impurities detected being traces of sodium and calcium. The melting point was 62.5°C.

This point was checked by means of differential cooling curves with thermo-junctions in potassium and aluminium. Very sharp, clear values were thus obtained with no variation whatever. 62.5°C agrees with the best values published for pure potassium.

It was not necessary to mount the specimens in vacuo. The molten metal, kept under "nujol" was drawn up into capillary tubes by suction, allowed to freeze, and the ends plugged with alundum cement and water glass to prevent running out when liquid. The curves, Fig. 6, indicate α and β modifications of the solid, the transformation occurring at about -120°C. Specimen (1), in which the heating was more rapid than

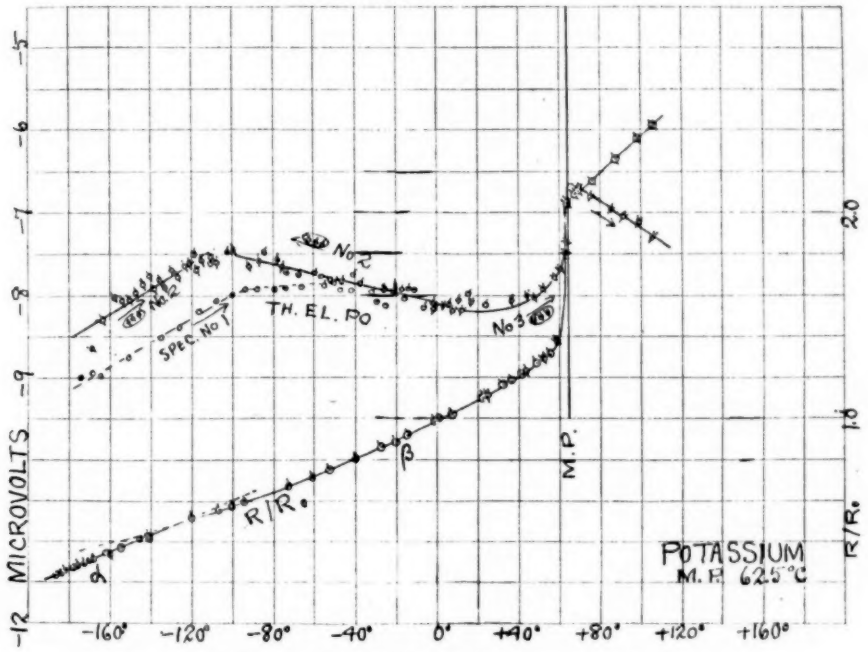

Fig. 6. Curves for potassium, m. p. 62.5°C.

with specimen (2), showed a rather gradual transition from the α to the β form. With specimen (2) the heating was very much retarded. The transition in this case appeared much sharper, occurring at about -110°C. The resistance line clearly indicates a change at about this point. The behavior on approaching the melting point is similar to that of caesium and rubidium. For specimen (1) the resistance at 0°C changed after the low temperature observations from 0.00700 to 0.00710. The zero value was unchanged after a second cooling to liquid air temperatures. After heating to $+55$° and cooling again to 0° the resistance changed from 0.00708 to 0.00697. After readings were taken

on the molten metal to 105°C the zero resistance was found to have increased to 0.00725. The specimen became blackened at this latter temperature. Repeated runs on the liquid metal gave parallel thermo-electric power lines slightly higher on successive runs, probably the effect of contamination.

Sodium

A sample of very pure sodium was obtained from Professor L. M. Dennis of the Department of Chemistry. Spectroscopic test showed only a trace of calcium. The melting point was determined as 97.0°C. The values given in Landolt-Börnstein agree at 97.5°C. Specimens were prepared for measurement following the procedure employed for

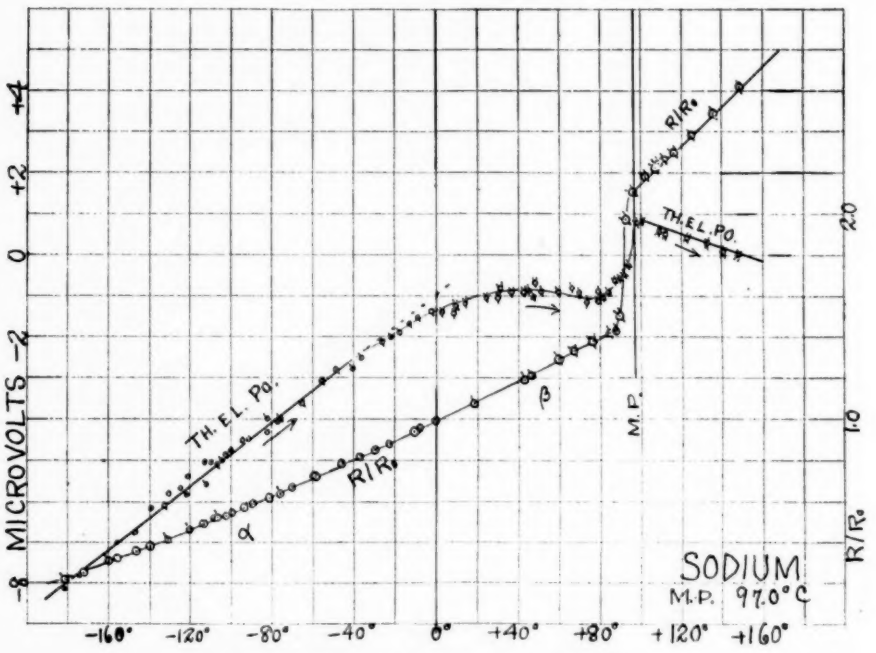

Fig. 7. Curves for sodium, m. p. 97.0°C.

potassium. The initial resistance at zero was 0.00755. After liquid air readings the value was 0.00753. After heating to +88° and back the value was 0.00752. After melting and heating to +150°C the zero value was 0.00760. Above −40°C, Fig. 7, the thermo-electric power points begin to deviate from the straight line followed from −180°C, suggesting a gradual transformation (obliteration of the lattice structure). At +80° the influence of approaching fusion is apparent. The resistance line does not show any break in this region. Successive runs on the

molten metal gave parallel thermo-electric power lines but with values each time slightly *lower* than the preceding, probably the effect of contamination.

Lithium

The lithium was prepared from c.p. lithium chloride by electrolysis of the fused salt. The chloride, obtained from the General Chemical Company and marked c.p., was found on spectroscopic test to contain a trace of sodium, with smaller traces of iron, magnesium and calcium. The metal as obtained by electrolysis showed only the trace of sodium, the other impurities being eliminated in the reduction. The electrolysis was carried on in a nickel crucible with an Acheson graphite anode and an iron wire with a loop in the end for a cathode. The electrodes were separated by a partition of quartz instead of the usual asbestos board which was found to introduce impurities. The melting point was determined as 183.0°C. Values given by Landolt-Börnstein are 180° (Bunsen 1855), 186° (Kahlbaum 1900), and 179° for the freezing point (Zukowsky; Masing and Tammann 1910).

The lithium metal was extruded into the form of a wire through an iron die. A piece about three inches long and 1/16 inch diameter was slipped into a quartz tube which it fitted closely. The constantan and platinum leads were pushed into the metal which was melted for this purpose for a few millimeters at each end by a Bunsen flame. The work on lithium was by far the most satisfactory as regards reproducibility on different runs and with different specimens. The quartz tube containing the metal wire was immersed in "nujol." On melting, capillarity was found to hold the liquid metal in the tube with no other constraint at top or bottom. Readings were thus obtained on thermo-electric power to 285°C, the metal still retaining its silvery luster at that temperature. Earlier readings on the molten metal in lead glass tubes had to be discarded on account of reaction with the glass. In quartz, however, no contamination occurred even at 285°C. Attempts were not made to run the temperature higher. The curves for lithium for both thermo-electric power and resistance, Fig. 8, shows very clearly a transformation at about +50°C.[3] There can be no question about the linear relation for thermo-electric power in this case, nor of the presence of α and β forms. The temperature range is sufficiently great to allow of no room for doubt and the closeness with which the points fit the lines on successive runs and with different specimens is quite remarkable. The black points or filled in circles represent data on a second specimen, the readings on which began at about 50°C and continued through change of state to

285°C and then back, the return indicated by the black points with tails. It will be noted that, even after melting and heating to 285° and freezing again, the thermo-electric power line was exactly duplicated except for a lag at the freezing point. The resistance line is perfectly straight from −190°C to +50°C. The deviation of the resistance line above 50°C is very definite. With the first specimen the resistance at 0°C was at first 0.00427, after the low temperature observations the value was 0.00428. A second specimen showed a zero resistance as .00417, and

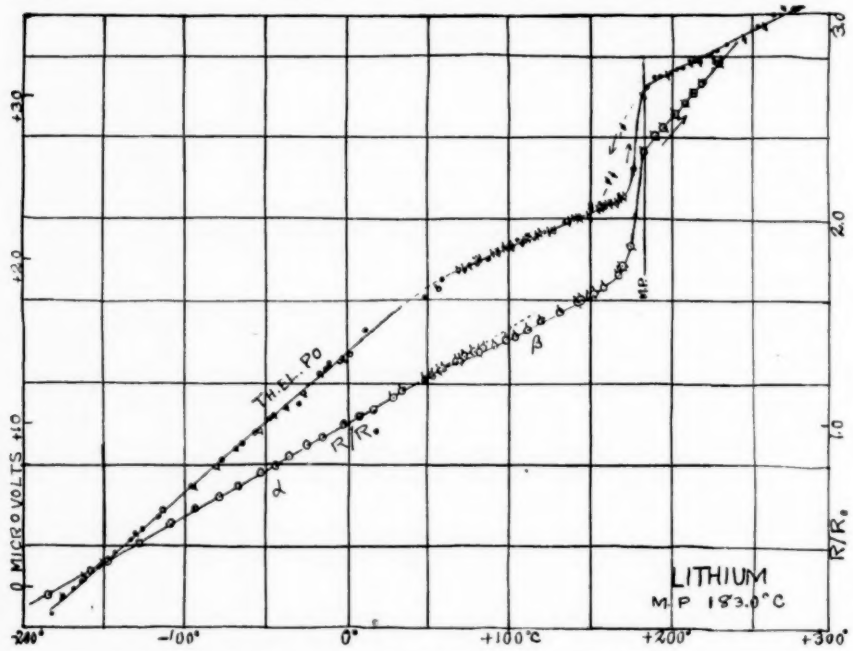

Fig. 8. Curves for lithium, m. p. 183.0°C.

still the same value after heating to +171°C. After fusion and heating to 230°C the resistance had increased to 0.00515. After melting in the tube and freezing again the specimen was found to fit the tube more loosely than originally. As the metal was much lighter than the "nujol" in which it was immersed, the effect of gravity and capillarity was apparently to cause a slight stretching with diminution of cross-section and consequent increased resistance. There was no oxidation or contamination.

General Discussion

Resistance. A comparison of the temperature coefficients of resistance found in this work with values reported by others should be of interest n view of the existing wide disagreement. Some of the lack of agreement

is probably due to ignorance of the transformations revealed by the present work. Likewise coefficients computed from data taken within 20° or 30° of the melting point would be very high and of little value for purposes of comparison. The values tabulated, Table I, give the coefficients through the ranges indicated. Thus α_{100} means the change in resistance per degree at 100°C divided by the resistance at 100°C.

TABLE I[4]

COMPARISON OF TEMPERATURE COEFFICIENTS AS DETERMINED BY VARIOUS OBSERVERS

	Bidwell	Bridgman	Northrup	Bernini	Hornbeck[5]
Lithium	0° to 50°C $\alpha_0 = .00457$ 50° to 150°C $\alpha_0 = .00380$ 200° to 300°C $\alpha_{200} = .00366$	0° to 100°C $\alpha_0 = .00458$		0° to 178°C $\alpha_0 = .00431$ 180° to 200°C $\alpha_{200} = .00206$	
Sodium (liquid)	20° to 75°C $\alpha_0 = .00530$ At 100°C $\alpha_{100} = .00425$	20° to 75°C $\alpha_0 = .00552$ At 100°C $\alpha_{100} = .00325$	20° to 93.5°C $\alpha_0 = .00530$ At 100°C $\alpha_{100} = .00330$	0° to 100°C $\alpha_0 = .00428$ At 100°C $\alpha_{100} = .00279$	6° to 88° $\alpha_0 = .00513$
Potassium (liquid)	0° to 50°C $\alpha_0 = .00553$ At 100°C $\alpha_{100} = .00375$	0° to 50°C $\alpha_0 = .00512$ At 95°C $\alpha_{95} = .00403$	0° to 50°C $\alpha_0 = .00580$ At 95°C $\alpha_{95} = .00342$	0° to 50°C $\alpha_0 = .00601$ 90° to 100°C $\alpha_{95} = .00358$	5° to 58° $\alpha_0 = .00552$

A comparison of the coefficients of resistance for the five metals at various temperatures as given by the writer's data is shown in Table II and graphically in Fig. 9. For the liquid metal the values have been corrected for the expansion of glass by assuming the cross-section increased by the fractional amount .00014 (twice the linear coefficient of expansion of lead glass). The coefficients of specific resistance would thus be greater than the observed values by this amount. The consistent decrease in the temperature coefficient of resistance with increasing atomic weight suggests a relation between these quantities.

TABLE II

Temperature Coefficients

	α_{-100}	α_{+100} (liquid)	α_0 (liquid)*
Lithium	.00820	.00599*	.01404
Sodium	.00730	.00440	.00758
Potassium	.00712	.00389	.00604
Rubidium	.00663	.00328	.00470
Caesium	.00638	.00244	.00311

* Extrapolated

[4] See summary of previous work on the alkali metals at the end of this paper for references and comments.

[5] Hornbeck, Phys. Rev. **2**, 217 (1913).

The coefficient for liquid rubidium is too high to fit the smooth curve upon which the other values lie. It should be noted that this value was obtained on the impure specimen, which melted at 33.0°C, the coefficient not being obtained for the purer specimen which melted at 37.2°C. This probably accounts for the discrepancy.

Thermo-electric power. Fig. 10 shows the thermo-electric power lines plotted to the same scale. The curves so plotted bring out interesting similarities in the thermo-electric behavior of sodium and potassium and

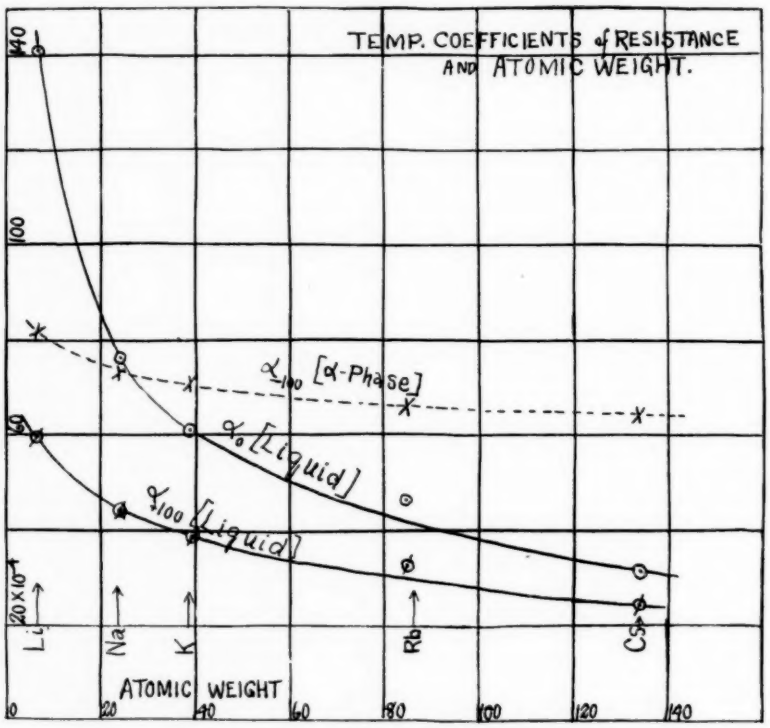

Fig. 9. Temperature coefficients of resistance as a function of atomic weight of alkali metal.

of rubidium and caesium. The lines for liquid sodium and potassium have very nearly the same slope. The same is true for the lines for liquid caesium and rubidium. Also the sodium and potassium lines have the same slope in the β form. The lead to platinum line is shown dotted, the line being taken for soft platinum from the paper of Tait.[6]

It is believed that the change in thermo-electric power at the melting point, as brought out by these curves, has never been clearly shown before. Richardson[7] says "we should expect these changes in electrical

[6] Tait, Trans. Roy. Soc. Edin., p. 125, 1873

[7] Richardson, The Electron Theory of Matter, p. 463

conductivity (on melting) to be accompanied by very considerable changes in the Peltier effect and in the thermo-electric power. Such effects have been looked for most carefully and with negative results."

The sign of the thermal e.m.f. was determined in all cases according to the usual convention, viz., if current flows across the hot junction from the metal being investigated to platinum, the metal is then said to be negative to platinum, i.e., regarding the junction as a source of e.m.f. the current then flows in the external circuit from platinum to the metal.

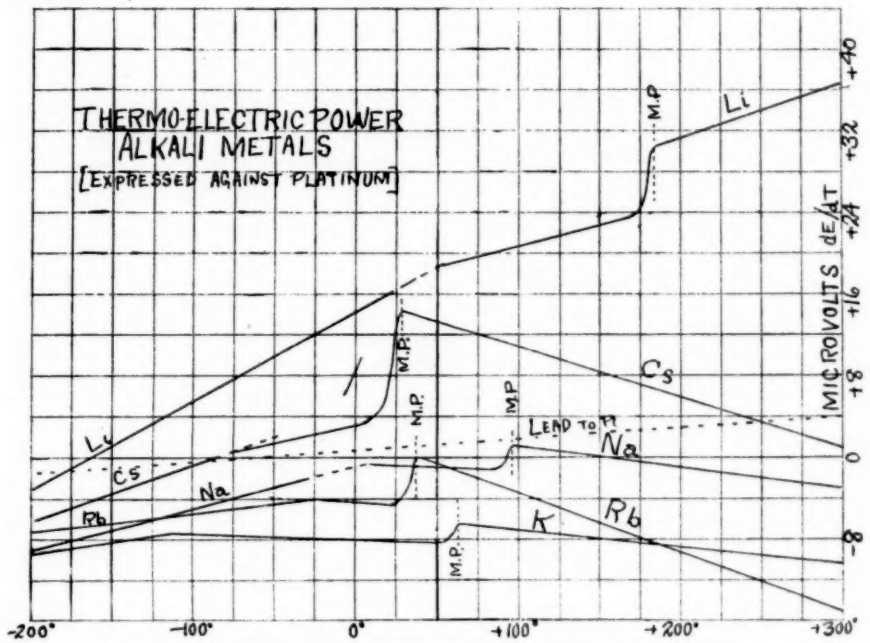

Fig. 10. Thermo-electric power of alkali metals against platinum.

The Specific Heat of Electricity

As originally shown by Lord Kelvin we may compute from thermo-electric data the so-called specific heat of electricity. It has been suggested by G. K. Lewis[8] that the excess atomic heat above the equipartition value, in the cases where that value is exceeded, is due to the acquisition of energy by the electrons, or the excess is the atomic heat of the electrons. Likewise Lewis has shown[9] that the electrons, even though their number equals that of the atoms, should not themselves have the equipartition value, that value being departed from because of the small mass and the constraints under which the electrons are held.

[8] Lewis, Proc. Nat. Acad. Sci. **4**, 25 (1918)
[9] Lewis, Phys. Rev. **4**, 331 (1914)

The expression for specific heat of electricity is obtained in the following way. From the First Law of Thermodynamics, assuming one of the metals of the couple to be lead,

$$dE = d\pi + \sigma dT \quad \text{or} \quad dE/dT = dT/dT + \sigma$$

where dE/dT is the thermo-electric power; π, the Peltier e.m.f.; σ, the Thomson e.m.f. per degree difference along the material. σ is the energy absorbed in carrying unit mass of electrons from a given point in the metal to a point one degree higher in temperature.

By application of the Second Law we have also

$$dE/dT = \pi/T \quad \text{or} \quad \pi = T\,dE/dT,$$

which when differentiated and combined with the above gives

$$\sigma = -T\,d^2E/dT^2.$$

The quantity d^2E/dT^2 may be obtained from the curves (Fig. 10) expressed in micro-volts per degree, per degree. When multiplied by T and by the factor .023074[10] we have σ in calories per degree per gram equivalent. The gram equivalent refers to the atomic weight in grams of the metal in question on the assumption that there is one electron available from each atom to share in the specific heat. A comparison of values of σ obtained from thermo-electric data with values computed from the excess in atomic heat has been made by Latimer[10] for a large number of elements. The more extensive data on the alkali metals afforded by the present work justify further comparison of the atomic heat of the electrons as computed in these different ways. Table III column (1) shows the slopes of the thermo-electric power lines, expressed in microvolts per degree per degree, and corrected to lead. Columns

TABLE III

Specific Heat of Electrons

	d^2E/dT^2			σ in calories		
	α	β	liquid	β (solid) At 20°C	liquid At 100°C	Observed excess of C_p over 6.4
Lithium	+.075	+.032	+.040	−0.216	−0.348	−0.53 at +20°C +0.88 at +100°C
Sodium	+.032	+.025	−.0282	+0.16	+0.24	+0.39 at +20°C
Potassium	+.009	−.0205	−.0275	+0.14	+0.23	+0.70 at +14°C
Rubidium	+.007	−.0205	−.069		+0.59	
Caesium	+.040	+.022	−.062		+0.53	

(2) and (3) show σ computed from these slopes. It is worthy of note that the values for sodium and potassium are nearly alike, as are also those of caesium and rubidium. There seem to be no data on the specific heats of the alkali metals in the liquid state although considerable

[10] Latimer, Am. Chem. Soc. Jour. **44**, 2136 (1922)

data for extreme low temperatures are available. Eastman and Rodebush[11] give for the atomic heat of sodium at 20°C (their highest value) $_aC_p = 6.79$, $_aC_v = 6.29$, and for potassium at +14°C, $_aC_p = 7.10$ and $_aC_v = 6.52$. The atomic heat of lithium $_aC_p$, according to Laemmel[12] has the following values; at 0°C, 5.56; at 50°C, 6.33; at 100°C, 7.28; at 190°C, 9.61. The thermo-electric data give the atomic heat at constant pressure. The average value of the atomic heat of the elements at constant pressure is 6.4. The excess above this rather than the excess over the equipartition value of 5.97 should probably be taken as giving the atomic heat of electrons. The excesses so computed from the available experimental data are given in column (4). Lindemann[13] computes 0.266 cal. as the atomic heat of the electrons at 27°C, a computation based on Debye's formula for specific heat, assuming the compressibility of the "electron space lattice" equal to that of silver. It is significant that the specific heat of electrons in the β form of lithium, sodium and potassium is nearly the same as in the liquid form; also that in the α form, the low temperature modification, the specific heat of the electron is negative in all cases. A negative σ is not unusual. It occurs in iron, nickel, platinum and other metals. The comparison afforded in Table III indicates that the heat capacity of the electrons as determined from thermo-electric data, assuming that we may properly interpret σ in this way, accounts for only a portion of the excess above the equipartition value. The fact that σ is sometimes negative needs interpretation.

A study of the crystal structure of the alkali metals at various temperatures is being undertaken with the hope of getting direct proof that the breaks in the thermo-electric power lines are due to crystalline modification as here assumed.[3]

CORNELL UNIVERSITY,
August, 1923.

Previous work on the alkali metals. The most extended observations on the temperature-resistance relations of the alkali metals are to be found in the papers of Bernini,[14] Northrup[15] and Bridgman;[16] and on thermo-electric properties in the work of Bernini,[17] Broniewski and Hackspill[18] and Barker.[19] For the resistance of caesium

[11] Eastman and Rodebush, Jour. Am. Chem. Soc. **40**, 498 (1918)
[12] Laemmel, Ann. der Phys. (4) 16, (1905)
[13] Lindemann, Phil. Mag. (6) **29**, 135 (1915)
[14] Bernini, Phys. Zeits. 1904, pp. 241, 406; 1905, p. 74
[15] Northrup, Trans. Am. Elec. Chem. Soc. **20**, 185-204, 1911; Jour. Franklin Jnst. **175**, 153-161, 1913
[16] Bridgman, Proc. Am. Acad. Arts. and Sci. 56-3, Feb. 1921
[17] Bernini, Nuovo Cimento, **15**, 29-42, 1908
[18] Broniewski and Hackspill, C. R. **153**, 814, 1911
[19] Barker, Am. Jour. Science (4) **24**, 159, 1907

and rubidium we have only the pioneer work of Hackspill,[7] Broniewski and Hackspill,[20] and Guntz and Broniewski.[21] The earliest work on the alkali metals is that of Matthiessen,[22] who made measurements on the resistance of sodium and potassium both on extruded wires and on specimens contained in capillary tubes. The measurements covered the range from 0° to 80° for potassium, and from 0° to 120° for sodium. He shows the large increase in resistance which occurs on change of state. His potassium melted between 46.8° and 56°, and therefore was not of high purity. His sodium was better, as its melting point was between 95.4° and 96.1°. The measurements of Bernini were more extensive. They were made on metals in capillary glass tubes immersed in oil. The observations for sodium and potassium were made through the range 0° to 130°, and for lithium through the range of 0° to 233°. Bernini's data do not agree with the observations of others, as indicated by the temperature coefficients, which have been tabulated for purposes of comparison, (Table I). His lithium melting point was 178°, indicating considerable impurity. His sodium melting point was good, yet his temperature coefficient (0°−100° range) is about 40 per cent lower than the values of others. He does not show sufficient data above the melting point to warrant a computation of the temperature coefficient of liquid sodium. His potassium melting point is about half a degree low, and the temperature coefficient (0° to 50° range) is considerably higher than that observed by others. Bridgman's measurements on solid lithium were made at four temperatures only, 0°, 25°, 50°, 75°, straddling a transformation region as indicated by the writer's data. His observations on molten lithium were made on an impure sample contained in a metallic capillary. On liquid potassium Bridgman made observations at three temperatures only. Bridgman's sodium melting point was 97.62°, indicating possibly better purity than my sample, which melted at 97.0°. The resistance data on caesium and rubidium are very meager consisting of a few observations between 0° and 40°, and at −78° and −183°. Low temperature readings on lithium, sodium and potassium likewise are recorded only for these two easily obtainable temperatures.

[20] Hackspill, C. R. **151**, 305, 1910
[21] Guntz and Broniewski, C. R. **147**, 1478, 1908
[22] Matthiessen, Phil. Mag. (4), **12**, 199, 1856; (4) **13**, 81, 1857

THE EFFECT OF CHANGES IN TOTAL CARBON AND IN THE CONDITION OF CARBIDES ON THE MAGNETIC PROPERTIES OF STEEL

By Arthur W. Smith, Edward D. Campbell and William L. Fink

Abstract

Variation of magnetic properties of a carbon steel and a chrome steel with per cent carbon, for annealed and quenched samples.—Two series of small steel bars were prepared with carbon varying from .01 to 1.17 per cent, one from Armco iron (total impurity .1 per cent or less), the other from chrome magnet steel with composition in per cent: Cr 2.23, Mn .24, Si .25, Ni .12, Cu .08, S .03, P .03. The carbon content was obtained and controlled by maintaining the bars along with steel of different carbide content until equilibrium was attained in hydrogen at 950°C. *Magnetization curves* are given for the different bars. The *minimum reluctivity R* (reciprocal of the *maximum permeability*) is found to be a linear function of the carbon content for hardened steels, to 0.8 per cent C. For annealed carbon steels, *R* increases somewhat faster than the per cent C and for annealed chrome steels *R* shows a maximum at about .5 per cent and a minimum at about 0.8 per cent C. The magnetic intensity necessary for saturation varies in the same way as *R*.

Magnetic potentiometer method of determining normal magnetization curves for short bars.—The bar and yoke apparatus used is arranged so that the small bar forms part of a closed magnetic circuit, and the magnetomotive force is distributed so as to be proportional to the reluctances of the bar and the yoke, respectively, by use of a magnetic potentiometer which consists of a solenoid of several thousand turns, with soft iron end plates which make contact with two points of the circuit. The magnetic flux was measured with a test coil connected to a dead beat ballistic galvanometer, by noting the deflection produced by reversing the flux. A special reversing rheostat was used to vary the current by 120 definite steps so as to give a definite magnetic cycle. Tested with samples of annealed Armco iron, this apparatus gave the same curve as the standard ring method.

IT has been recognized for many years by chemists and metallurgists that carbon is the essentially characteristic element which distinguishes all steel from iron, and that carbon in steel occurs chemically combined as a carbide either of iron alone or with more or less of the iron replaced by other elements. Some of these, such as chromium, tungsten, molybdenum, vanadium, and manganese, form with iron double carbides which have a very marked difference in their influence on the properties of steel from those produced by the carbides of iron alone. The properties of steel are also influenced by the heat treatment to which the steel has been subjected. If the steel is heated above the critical range, the carbides pass into solution and may be largely retained in this condition

by rapid cooling through the critical range, as in water hardening. If, however, the metal is slowly cooled through the critical range, as in annealing, most of the carbides precipitate, leaving a relatively small proportion of the carbides in solution. The concentration of carbides remaining in solution after annealing will depend on the total carbon content and the constitution of the resulting carbides.

The effect of changes in carbide concentration on the magnetic properties of some heat treated carbon steels has been studied[1] by means of a special magnetic balance designed by one of the authors. The object of the present investigation is to extend our knowledge of the effect of changes in carbide concentration on the magnetic properties of steel by a more precise method,[2] using a magnetic potentiometer designed by A. W. Smith.

For this work two series of small steel bars were prepared and heat treated in the chemical laboratory. One series was prepared from Armco iron, furnished by the American Rolling Mill Company, and the other from a sample of chrome magnet steel furnished by the Penn Seaboard Steel Corporation. Each series consisted of bars containing four different carbon contents. The bars of each series having the lowest carbide content were produced through decarburization by means of the action of hydrogen at 950°C.[3] The carbide content of the other bars was varied by maintaining them in a still atmosphere of pure dry hydrogen at 950°C, together with steel of different carbide content, until equilibrium had been reached.[3]

The annealing of all bars was effected by allowing them to cool from 950°C over night with the furnace in which they were prepared. The hardening was effected by suspending a number of bars for one hour in an electrically heated furnace which had been brought to the temperature from which it was desired to quench the bars, and then quenching them in a large volume of water at 25°C. The temperature of the bars at the moment of withdrawal from the furnace was measured by means of a standard platinum-platinrhodium thermocouple, the bead of which was within 2 or 3 mm of the bars under treatment. The upper half of the heating chamber in which the bars were suspended, consists of nichrome wire gauze and is surrounded with charcoal so that the bars may be maintained for any desired length of time without any sign of oxidation. Bars A, B, C, and E were quenched from 915°C while D, F, G, and H were quenched from 885°C in order to ensure homogeneity.

[1] E. D. Campbell and E. R. Johnson, Jour. Iron and Steel Inst., 1922, No. 2, p. 201

[2] Arthur W. Smith, Phys. Rev. **19**, 424 (1922)

[3] Details were reported to the Iron and Steel Institute, Autumn Meeting, Sept. 1923

The chemical composition of the steels prepared for this work is given in Table I.

Unfortunately for magnetic testing, these steels are all in the form of short bars, 15 cm in length and 6 by 6 mm in cross section. They are a part of a set comprising several hundred bars of similar dimensions

TABLE 1

Composition in weight percent of the prepared steel bars

Steel bars	C	Mn	P	S	Si	Cr	Ni	Cu
A16 and A11	.008	.011	.006	< .018				.018
B1 and B4	.33	.024	.005	.023	trace			.042
C22 and C23	.41	.016	.005	.03	trace			.045
D3	.70	.016	.005	.03	trace			.045
D5	.70	.011	.006	.018				.018
E10 and E13	.04	.24	.027	< .035	.25	2.23	.12	.084
F1	.55	.24	.027	.035	.25	2.23	.12	.084
F2	.52	.24	.027	.035	.25	2.23	.12	.084
G19 and G29	.85	.24	.027	.035	.25	2.23	.12	.084
H25 and H27	1.17	.24	.027	.035	.25	2.23	.12	.084

accumulated during the past ten years by one of the authors in the course of his researches on the constitution of steel. For magnetic testing the ring form is much better as it gives a uniform magnetic circuit and the uncertainties due to the ends of the bars do not appear.

Inasmuch as it is difficult to confine the magnetic flux to a prescribed circuit without serious leakage, it seemed best to build a bar and yoke apparatus in which the m.m.f. would be applied bit by bit along the entire circuit, being distributed over each part in proportion to the reluctance of that part. This arrangement avoids the uncertainties due to magnetic leakage.

The bar and yoke apparatus. The arrangement of the magnetic circuit is shown in Fig. 1. *AB* represents the bar to be tested. Each end of this bar is tightly clamped into the yoke of common iron that completes the

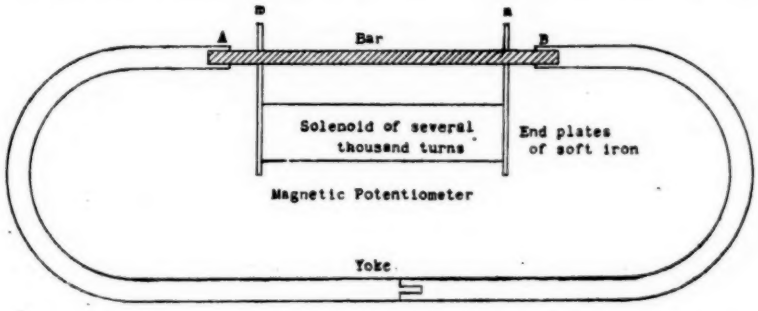

Fig. 1. Bar and Yoke, giving a closed magnetic circuit. The "magnetic potentiometer" is shown, connected to the bar.

magnetic circuit. The square bar is held by hollow square jaws that make contact for about a centimeter length along the bar. If the bar is not absolutely square, good contact is assured on at least two sides of the bar. There is another joint at the middle of the yoke. The reluctance of the circuit is thus made up of three parts, that of the bar, of the yoke, and of the joints.

The magnetizing coils. Surrounding the bar are three brass spools, a long one in the middle and a short one at each end, with a space of 3 mm at m and n, the reason for which appears below. These spools carry a uniform winding of p turns per cm, with additional turns at each side of m and n equal to the number of turns that should have been placed in these openings to make the winding uniform throughout. These coils are permanently connected in series and carry the current that magnetizes the bar.

Over the entire length of the yoke is another uniform winding with additional turns over each joint proportional to the extra reluctance at these places. The current through this winding is independent of that around the bar, and it is adjusted to the value necessary to magnetize the yoke to the same total flux as exists in the bar. Under this condition the magnetic flux is continuous through the bar and the yoke, the same as though the circuit were of uniform material and magnetized by a single current I in a uniform winding of p turns per cm.

Measurement of magnetic flux. The magnetic flux was measured by the deflection of a Leeds and Northrup high sensitivity ballistic galvanometer, arranged as a deadbeat fluxmeter and critically damped by a circuit of 70,000 ohms. When joined to a low resistance, as in the present case, the galvanometer is practically shortcircuited and it is so greatly over damped that it stands nearly at rest on any part of the scale, drifting back only slowly towards the zero position.

The test coil consisted of 50 turns of fine copper wire wound on the middle of the long brass spool before the primary winding was put on. It therefore encircles the middle of the bar and includes a minimum of the surrounding space. When the magnetic flux is reversed the galvanometer gives a quick swing and comes to rest at the end of the deflection. It is not difficult to read this position on the scale, as the drifting is very slow, but a more exact reading is taken. The scale, as seen in the reading telescope, is watched until one of the lines comes squarely under the vertical cross hair of the telescope. This coincidence can be determined more exactly than an intermediate position between two lines. At this instant the magnetic flux is reversed again, deflecting the galvanometer back to the zero position, or a little beyond. There is now no

tendency even to drift, and the reading can be determined under stationary conditions. Moreover, if there is any time lag of the magnetic flux the reading can be deferred without error until the flux has reached its full value.

The reversing rheostat. When an inductive circuit is suddenly broken it is not possible to tell how the current will vary as it dies down to zero. The spark shows the high value of the induced e.m.f. that tends to keep the current flowing, and in some cases the current may even oscillate a few times before the energy of the magnetic field is dissipated. In such a case the magnetic cycle of the iron may differ widely from the regular hysteresis loop when the current is gradually reduced to zero.

In order to avoid the possibility of this uncertainty in the cycle through which the iron is carried, and also to make the changes slowly and regularly so as to avoid any violent and sudden impulses on the galvanometer, the magnetizing current was varied by a special rheostat. By turning the movable arm of this rheostat, resistance was introduced into the circuit sufficient to bring the current to zero during the first quarter turn. At this point the next step reversed the battery connections, and then the resistance was gradually cut out of the circuit during the next quarter turn. Thus by merely swinging the arm of the rheostat through a half turn and back again, the magnetizing current is changed through one cycle from $+I$ to $-I$ and back to $+I$ in 120 steps. Each step gives a small impulse to the galvanometer which thus reaches its maximum deflection without any sudden shock. This feature is especially desirable when the galvanometer is being calibrated by reversing the current in a standard of mutual inductance.

The magnetic potentiometer. The total m.m.f. applied to the magnetic circuit is easily computed by the formula $4\pi NI$, but how much of this is used for the bar and how much for the rest of the circuit? The case is similar to that of an electric circuit composed of alternate resistances and batteries. The total e.m.f. drives the current through the total resistance, but the batteries in a given portion, AB, may not furnish all of the e.m.f. that is used in this portion of the circuit. Whether they do or not could be determined by connecting a voltmeter to A and B. If the voltmeter indicates no difference of potential between these points it shows that the fall of potential RI in this portion of the circuit is just equalized by the e.m.f. of the batteries in this portion.

The magnetic potentiometer, corresponding to the voltmeter, consists of a coil of several thousand turns of fine wire wound on a fibre core. The ends of this solenoid are supplied with flat pieces of soft iron that extend on one side far enough to be clamped against the test bar

at m and n. If there is a difference of magnetic potential between these points some flux will be shunted from the bar to the circuit through this coil,[4] and when the flux is reversed it can be detected by the galvanometer. If there is no difference in magnetic potential between two points on a magnetic circuit when a m.m.f. of $4\pi NI$ gilberts is applied to the circuit between them it shows that just this amount of m.m.f. is required to maintain the flux through this portion of the circuit. The number of gilberts per cm required along this part of the circuit is, then,

$$H = 0.4\pi pI_a$$

where pI_a denotes the number of ampere-turns per cm.

Usually the adjustment is made by setting the current around the bar at a given value, and then varying the current in the winding around the yoke until, after many reversals of both currents, there is no change of flux through the coil of the magnetic potentiometer. It is then a simple matter to shift the galvanometer connections to the test coil around the bar and measure the corresponding value of the flux through the bar.

Test of the bar and yoke. The bar and yoke method described above was compared with the standard ring method by determining the normal magnetization curves for a bar and a ring of Armco ingot iron, both of which had been annealed together so as to be as nearly alike as possible. Each method gave the same curve, even more closely than could well be expected from two samples of the same iron by either method.

Calibration of the galvanometer. The galvanometer was calibrated by means of a standard of mutual inductance, the secondary of which was kept in the galvanometer circuit. When a calibration was desired a known current was passed through the primary and reversed by means of the same reversing rheostat as was used for the bar and yoke. For the range of deflections used in this work the scale deflection is very closely proportional to the flux cut by the galvanometer circuit.

Comparison of the steels. The normal magnetization curves showing the relation between the flux density B, in maxwells per cm^2, and the magnetic intensity H, in gilberts per cm, are given in Figs. 2, 3, 4 and 5. These curves are drawn accurately to scale, and the observed points are all covered by the width of the line.

An increase in the percentage of carbon increases the amount of the carbides in solution, and this decreases the magnetic permeability of the steel. This lessened permeability is probably due to some asymmetry of the iron atoms, making it more difficult for the magnetons to align themselves in the direction of the magnetic field. This would be expected

[4] See A. P. Chattock, Phil. Mag., **24**, 94, 1887

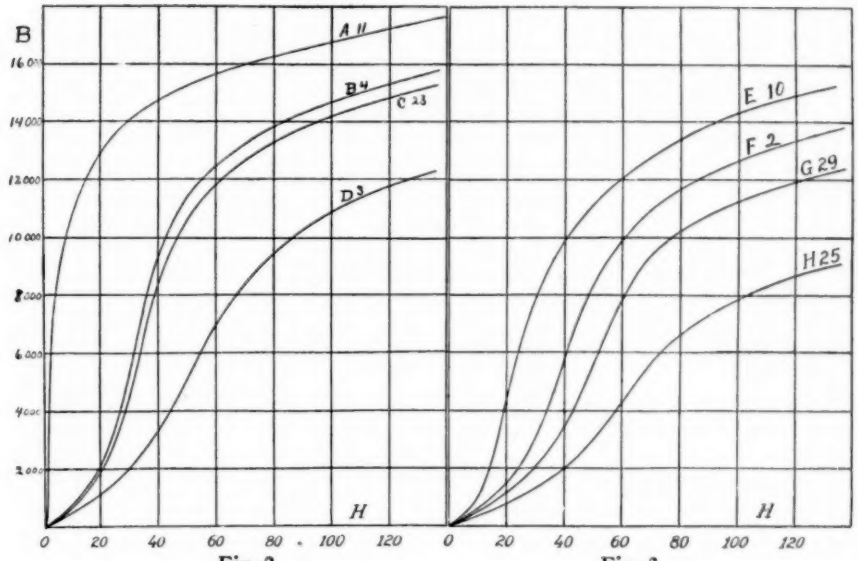

Fig. 2 Fig. 3

Fig. 2. Hardened carbon steels, showing the normal magnetization curves with different percentages of carbon.

Fig. 3. Hardened chrome steels. Showing the normal magnetization curves with different percentages of carbon.

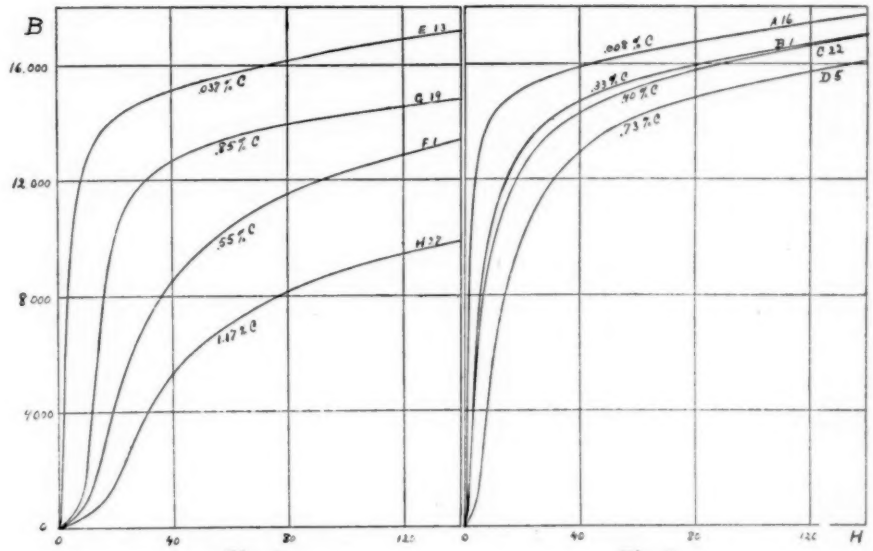

Fig. 4 Fig. 5

Fig. 4. Normal magnetization curves for the annealed bars of chrome steel, with varying carbon content.

Fig. 5. Normal magnetization curves for the annealed bars of Armco iron with varying amounts of carbon added.

to require a greater value of the applied magnetic field to produce a given degree of magnetization. The maximum value of the permeability, or the minimum value of the reluctivity, for a given steel is attained under the conditions in which the magnetons within the atoms of iron are most free to add their magnetic effect to that of the applied field. The curves marked *H* in Figs. 6 and 7 show the relation between the percentage of total carbon and the values of *H* that will bring the corresponding steel to this condition of maximum permeability. For the hardened chrome steels this relation is linear, and it is nearly so for the carbon steels. The curves marked R show the corresponding relation between the minimum value of the reluctivity and the percentage of carbon. These curves are linear except for the last point in Fig. 7.

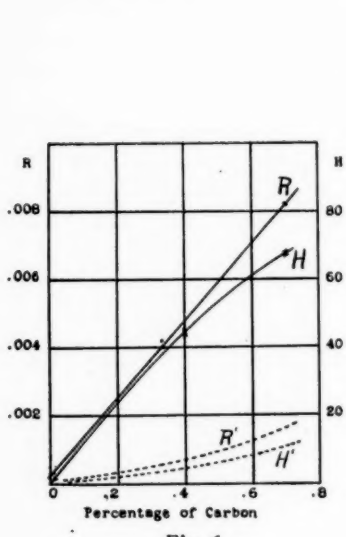

Fig. 6

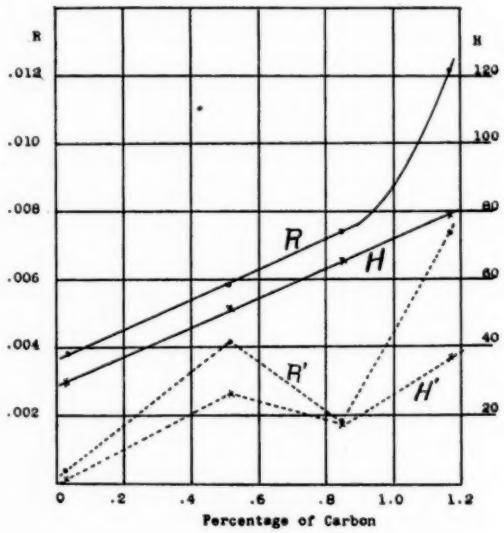

Fig. 7

Fig. 6. Hardened carbon steels. Curve R shows the minimum values of the reluctivity for varying carbon content. Curve H shows the values of *H* necessary to bring the steels to the point of maximum permeability. Curves R′ and H′ show the corresponding values after the steels have been annealed.

Fig. 7. Hardened chrome steels. Curve R shows the minimum values of the reluctivity of the different steels for varying carbon content. Curve H shows the values of *H* necessary to bring the steels to the point of maximum permeability. Curves R′ and H′ show the corresponding values after the steels have been annealed. Note the drop in these curves at .8 per cent carbon.

Prof. J. A. Ewing has recently suggested[5] a model for the iron atom in which an inner group of electrons may act as an elementary magneton. In pure iron this magneton can turn easily and align itself with the

[5] J. A. Ewing, Proc. Roy. Soc. Edin. **42**, pp. 97-128, 1922

magnetic field, but in alloys, solid solutions, or compounds, the atom is under non-symmetrical forces and the magnetons are less free to follow the external field.

In the annealed bars the carbides have had ample opportunity to separate out of the solid solution, and therefore the effect of the carbon is much less. This is shown by the corresponding curves (dotted lines) at the bottom of each figure. In the case of chrome steel a very striking effect appears for .85 per cent of carbon. This steel behaves like a steel of much smaller carbon content, having a maximum permeability over twice as large as the steel with .52 per cent carbon. This effect does not appear in the straight carbon steels, and is due to a combination of the chromium and carbon that in effect removes some of each of these elements from the iron. Beyond this point, with the chromium largely combined with the carbon, the excess of carbon produces its normal effect of increasing the reluctivity of the steel.

PHYSICS LABORATORY
UNIVERSITY OF MICHIGAN,
September 18, 1923.

SOME NEW STANDARD MELTING POINTS AT HIGH TEMPERATURES

By Howard S. Roberts

Abstract

Melting points of salts for use as standard temperatures for thermocouples, 400° to 1100°C.—After purification by crystallization from solution, a gram of the salt is placed in a Pt crucible 18 mm by 10 mm in diam., the junction is placed in the axis and 3 to 4 mm from the bottom, and the temperature is raised about 5° per minute. For most pure substances and certain eutectics the heating curve becomes quite flat at the melting point and hence the form of curve obtained is a sensitive test of purity. The couples used were carefully calibrated with standard metals, and gave the following results, accurate to ±0.5°: *potassium dichromate* 397.5°; (30.5 $NaCl$+69.5 Na_2SO_4) 627.0°; KCl 770.3°; $NaCl$ 800.4°; Na_2SO_4 884.7°; K_2SO_4 inversion point 583±1°, melting point 1069.1°; also $Ca_2B_2O_5$ 1304±5°. Detailed suggestions as to technique are given, also a *convenient method of using pure metal strips or wires in calibrating couples.*

THE fixed points by means of which the high temperature scale is at present reproduced are for the most part the melting points of pure metals. While these leave little to be desired by way of reproducibility, it is often inconvenient or impossible to use them directly for the calibration of a thermometer under its everyday working conditions. Furthermore there is also a need for a series of easily obtainable materials which may be used without purification for a moderately accurate calibration. It is the purpose of this paper to present a series of salts which may be employed for calibrations of moderate accuracy without purification, or may be carefully purified and used for an accurate calibration. The series is intended primarily for the calibration of thermocouples.

The use of salts as standards has been objected to on the ground that their low thermal conductivity makes them less accurate than the metals. This is not because the salts are necessarily less able to reproduce their melting points accurately but because of the limitations of the thermometers and of the methods used. It is particularly the case where a large volume of the thermometer must be in contact with the melting salt; but it must be remembered that, with the exception of the resistance thermometer, such instruments are seldom used for precise measurements at high temperatures. On the other hand, in the calibration of optical pyrometers, fine wire thermocouples, etc., the effect of low conductivity can be made negligible by the employment of a suitable technique, and

here a suitable series of salts will be found quite as satisfactory as a series of metals. The fact that there are so many salts to choose from makes it possible in most cases to obtain fixed points at short intervals and to confine the choice to those salts which are easily purified.

In a paper on "Melting point determination" White[1] has called attention to the remarkably sharp melting curves obtained with certain substances, notably sodium chloride and sodium sulphate. His discussion of the causes for obliquity in the melting curve makes it evident that only under very unusual conditions can such a sharp melting curve be obtained with any but an "ideally pure"[2] substance, and that such a curve represents the constant melting temperature of the substance in question. In the form of the melting curve we have, therefore, an almost infallible check on the purity of such a salt and on the reliability of any given determination with it.

With one exception the salts were chosen from standard chemical reagents with the restriction that they must be easy to purify by simple methods. As will be brought out later, this purification will nearly always be found advisable, if only to get rid of the inevitable dust, paper, and bits of wood.

The melting curves were obtained with powdered charges, in a crucible 10 mm in diameter and 18 mm deep, using a bare thermocouple whose junction was located as nearly as possible in the axis of the crucible and

TABLE I

Fixed points used in the calibration

Substance	Source	Melting point	Authority
Lead	Bur. of Stds. Std. sample No. 49	327.3°	Bur. of Standards[4]
Zinc	Bur. of Stds. Std. sample No. 43a	419.4	Bur. of Standards
Aluminum	Bur. of Stds. Std. sample No. 44	658.7	Bur. of Standards
Gold	Heraeus	1062.6	Day, Sosman, Allen[5,6]
Lithium metasilicate	Synthetic	1201.	Day, Sosman, Allen[6]
Palladium	American Platinum Works	1551.5	L. H. Adams[7]

[1] White, Am. J. Sci. **28**, 453, 1909; also J. Phys. Chem. **24**, 393-416, 1920

[2] For our purpose an "ideally pure" substance is to be defined as any solid or mixture of solids that is free from melting hysteresis and gives, on melting, a liquid whose composition remains constant throughout the melting interval. This definition is worded in such a way as to include eutectic mixtures and certain cases of transformation and of solid solution. It does not, however, apply to most of the silicates.

[3] L. H. Adams, J. Am. Chem. Soc. **36**, 65-72, 1914

[4] Bur. Standards Circ. 66 (1917)

[5] Day, Sosman and Allen, Am. J. Sci. **33**, 587 (1912)

[6] Day, Sosman and Allen, Carnegie Institution Publ. No. 157 (1911); J. de Phys. (5) **2**, 911, (1912).

[7] This lot was found by Adams to melt 2° higher than the standard palladium.

3 to 5 mm above the bottom. The thermocouple was standardized at the melting points given in Table I, using a method to be described below. An electric furnace wound with resistance wire was used for heating, the rate being about 5° per minute.

The deviation curves for the three couples used are given in Fig. 1. They represent the difference between an arbitrary standard curve[3]

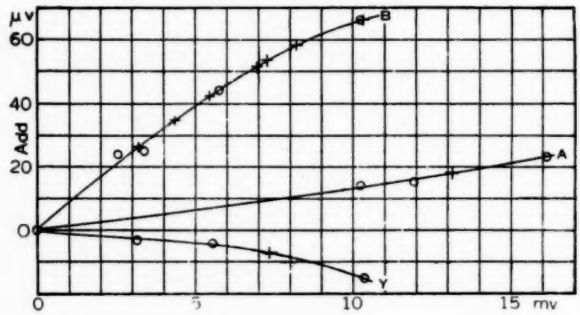

Fig. 1. Calibration curves for the three couples used. The circles represent melting points used in the calibration (Table I); the crosses, melting points determined with the couple (Table II).

of temperature and e.m.f., and the observed values of e.m.f. at the melting point, plotted against the observed value. Element A was used for the

TABLE II

Melting points of the purified salts

Substance	Melting point	Probable accuracy	Microvolts[8]
Potassium dichromate	397.5°C	±0.5°	3220
45KCl+55Na_2SO_4 by weight[9]	517.1	±1.0°	4385
30.5NaCl+69.5Na_2SO_4 by weight	627.0	±0.5°	5499
Potassium chloride	770.3	±0.5°	7008
Sodium chloride	800.4	±0.5°	7335
Sodium sulphate	884.7	±0.5°	8262
Potassium sulphate[10]	1069.1	±0.3°	10372
Dicalcium borate[9] ($Ca_2B_2O_5$)	1304.	±5°	13176

dicalcium borate point, B for all the others, and Y as a check at the sodium chloride point.

[8] According to Adams' standard curve, J. Am. Chem. Soc. **36**, 68, 1914; Bull. Am. Inst. Mining Met. Eng., 159, 2114. 1919; Pyrometry Volume, Am. Inst. Mining Met. Eng., p. 168, 1920; reprinted in Bur. Standards Tech. Paper 170, 308. 1921.

[9] Give more or less oblique melting curves

[10] Potassium sulphate passes through a sharp inversion at 583° ±1° which may be used to obtain a second calibration point with a single charge. This point, together with the melting point of potassium sulphate will often be sufficient for a complete calibration.

The results for the purified materials are given in Table II, and the melting curves are shown in Figure 2.

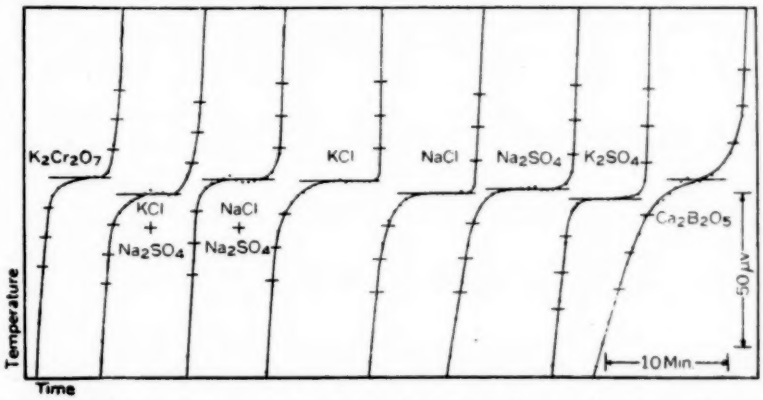

Fig. 2. Melting point curves for the various salts after purification. Short, horizontal lines are drawn through the curves at intervals of 1° above and below the melting point.

The column headed "probable accuracy" gives the maximum departure to be expected from the scale as defined by the fixed points listed in Table I.

The mixture of potassium chloride and sodium sulphate is an approximation to the ternary eutectic[11] $(43Na_2 \cdot 57K_2)$ $(46Cl_2 \cdot 54SO_4)$. The eutectic composition may be obtained more accurately by mixing 44.5% KCl, 2.5% NaCl, 53% Na_2SO_4 or 37% NaCl, 11% Na_2SO_4, 52% K_2SO_4 by weight; but the melting point so obtained does not differ materially from that of the mixture given in Table II.

The melting point of sodium chloride was measured several times with particular care. It is given by White[12] as 801° ±1°, but a more recent determination by Ferguson[13] gives 803° ±1°. This difference of 2° seemed rather more than could be explained by the uncertainty of the temperature scale or of the standard calibration curve for the platinum-platinrhodium thermocouple. Therefore, through the courtesy of Dr. Day, "Element Y," which had been compared with the gas thermometer by Day and Sosman[5] was used to check the interpolation between the fixed points. For this purpose a calibration of Element Y was made at the melting points of potassium dichromate, the sodium chloride-sodium sulphate eutectic, and potassium sulphate. The melting point of sodium chloride then obtained with this couple was 800.4°, in entire agreement

[11] Jänecke, Z. phys. Chem. **64**, 351, (1908)
[12] White, Am. J. Sci. **28**, 470, (1909)
[13] Ferguson, J. Phys. Chem. **26**, 626, (1922)

with that obtained by the use of Element B. The value in Table II of 884.7° for sodium sulphate is in satisfactory agreement with White's[12] value 885° ± 1°. There seems, therefore, to be little doubt that Ferguson's[13] 803° for the sodium chloride point is too high.

The desirability of potassium sulphate as a fixed point has been known for some time; but it has been suspected of having two or more dimorphous forms with different melting points,[14] as is the case with sulphur. No evidence was found to support this belief; two such forms are indeed known, but the transformation from one to the other takes place with unusual promptness at 583°. It seems unlikely that the whole, or even any considerable portion of a powdered charge should remain in a metastable condition; and should it consist of a mixture of dimorphous varieties, the melting point curve would of necessity be oblique except in the remote contingency of the formation of a eutectic mixture of the two forms. On the other hand, a reason for the earlier uncertainty is to be found in the high temperature at which this salt melts, which makes the observed melting point particularly susceptible to impurity in the salt and to various defects in the method of measurement.

Factors Influencing the Shape of the Melting Curve

While the melting curve obtained under satisfactory conditions with an "ideally pure" substance is unmistakable, it may be well to consider the more common causes of variations from the normal curve, for by so doing we may know when to eliminate the cause and when the effect may be ignored.

The curves of Fig. 3 are hypothetical time-temperature curves for the melting of an ideally pure substance, assuming a linear heating rate for the furnace, a long, cylindrical charge of small diameter and no change in the size of the charge on melting. Curve *a* gives the temperature at the center of the charge, *b* at a point near the center, and *c* at the surface. Since the heating rate is linear, the small charge quickly reaches a steady state in which all parts of the charge have the same heating rate. This linear rate and temperature distribution continue unchanged until the instant t_1, when the hottest portion (the surface) of the charge reaches the melting temperature. The linear rate for the unmelted interior now becomes a decreasing rate, approaching the constant melting temperature. The time lag through the charge is usually so small that the temperature at the center becomes sensibly equal to the melting temperature within a much smaller fraction of the melting interval than is indicated in the figure. As soon as melting passes any point *b* in the interior, the tempera-

[14] Burgess and Le Chatelier, The measurement of high temperatures, p. 451 (1912).

ture at this point immediately begins to rise; at the instant t_2 when it reaches the center the temperature there rises very rapidly and the charge as a whole approaches a new steady state, somewhat different from the first on account of changes that have taken place in the thermal conductivity and specific heat.

Aside from the effect of impurity which White[1] has discussed elsewhere, the most common variation from the normal is curve *b*, caused, usually, by an error in centering the junction. This is evident in the curve for sodium sulphate in Figure 2. It need cause no concern if the horizontal portion is very well defined. Small fluctuations of temperature may be caused by local heat effects involving bits of foreign matter in the charge or, at the beginning of melting, by imperfect thermal contact between the charge and the thermocouple. If the charge is placed too high in the

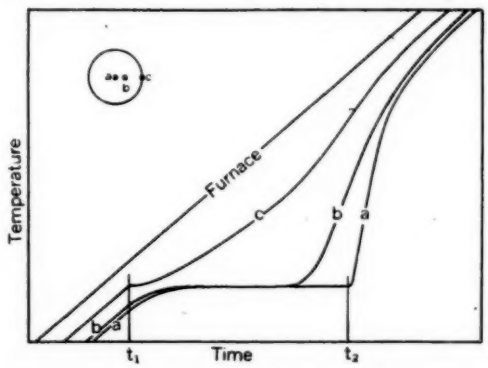

Fig. 3. Hypothetical time-temperature curves for different parts of a cylindrical mass of an "ideally pure" substance melting under idealized conditions. *a* at the center of the cylinder; *b* at a point within, but not at the center; *c* at the surface.

furnace the bottom may melt first and subsequently bits of unmelted material fall into the melt from the top; these may give rise to a false start toward the sudden rise at the end, as is the case in the curve for sodium chloride in the figure.

If the thermocouple has been rendered inhomogeneous by contamination, its indications may change while the gradient along it is changed during the melting interval. This may cause the flat portion of the curve to slope either up or down, giving an erroneous idea of the purity of the salt. The effect of this on the calibration will probably not be greater than the uncertainty inherent in the use of the contaminated couple; it may be reduced by employing a slow heating rate.

In general, given a suitable, pure salt, and a good thermocouple well centered in the charge, the melting curve should not be very different from *a* in Fig. 3. If such a curve is not obtained, the foregoing discussion,

together with White's discussion of the effect of impurities, should be sufficient to locate the cause.

Dicalcium borate in my table and the silicates in that of Day, Sosman, and Allen fail to conform to our definition of an ideally pure substance and our discussion does not apply to them. In using such salts it is suggested that particular care be taken in centering the thermocouple and that the heating rate be slow. If there is any uncertainty about either the technique or the homogeneity of the thermocouple, these may be checked by a calibration at one of the other points.

Suggested Technique for Bare Thermocouples

The size of crucible used here, 10 mm in diam. and 18 mm deep, will probably be found most satisfactory for the calibration of thermocouples not more than 0.6 mm in diameter (No. 22 B & S wire gage). It is large enough to allow a leeway of a millimeter or so in centering the junction and small enough to avoid too much rounding of the ends of the melting curve. For the large wires of the usual base metal couples the crucible should be much deeper, in order to provide sufficient depth of immersion, and somewhat larger in diameter. The minimum thickness of salt outside the thermocouple need not be much more than 5 to 10 mm.

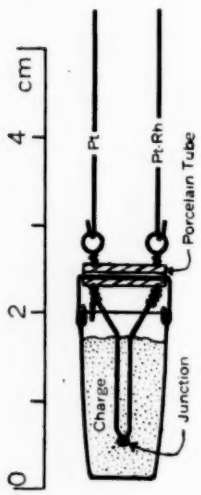

Fig. 4. An arrangement which has proven satisfactory, in the calibration of thermo-couples, as a container for the melting salt.

For a great deal of our work with platinum-platinrhodium couples we have found the arrangement shown in Figure 4 very satisfactory.[15] A short tip is made of the thermocouple wires, terminating in eyelets at the top and hung on a cross bar of porcelain tubing. The crucible has two small holes drilled opposite each other near the top and is supported by a bent platinum wire which passes through these holes and through the porcelain tube. The thermocouple to be calibrated is cut apart at the junction and the crucible hung from it by means of the eyelets, taking care that the wires are not interchanged.

In many cases it will be found convenient to melt the salt cautiously over a Bunsen burner, adding more salt until the crucible is nearly full. The thermocouple may then be thrust into the melt and the salt allowed

[15] Smyth and Roberts, J. Am. Chem. Soc. **42**, 2589, 1920

to freeze around it, after which it is placed in a furnace for the melting point determination. This preliminary melting is not to be recommended for exact work on account of the danger of partial dissociation or contamination of the salt.

These salts (with the exception of dicalcium borate) are very soluble in water, so that the crucible may be cleaned out after a determination, by washing. Dicalcium borate is readily soluble in dilute hydrochloric acid (equal parts of acid and water) especially on heating.

Preparation of the Salts

The curves of Figure 5 indicate forcefully both the desirability of purifying the salts, and the seriousness, for exact work, of even small amounts of impurity.

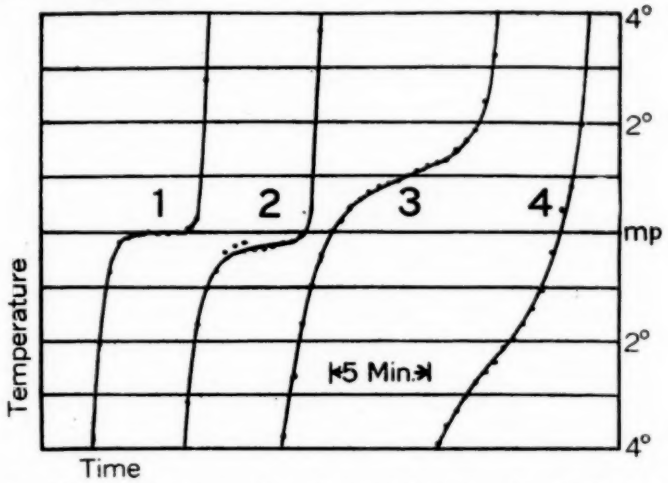

Fig. 5. Melting point curves for sodium sulphate showing the effect of impurities. The horizontal lines are drawn at intervals of 1° above and below the melting temperature (884.7°). (1) purified material; (2) as received from the manufacturer; (3) with the addition of 0.5% $CaSO_4$ to show raising of the melting point; (4) with the addition of 0.3% NaCl to show lowering of the melting point.

The chief impurity met with in these salts has been dust and foreign matter of various sorts, and when these were removed by dissolving the salt and filtering the solution, a single recrystallization was sufficient. With the exceptions of sodium chloride and potassium dichromate, as much of the salt as possible was dissolved in boiling water, the solution filtered and allowed to cool.[16] The liquid was then poured off and the

[16] Sodium sulphate has a maximum solubility at about 32°. It is therefore advisable to cool the solution considerably below this temperature, e.g., in an ice bath, in order to obtain a reasonable quantity of the solid from it. The decahydrate so obtained melts about 32° and the liquid should then be evaporated to dryness rather cautiously in order to avoid undue loss by spattering.

remaining crystals tamped with a glass rod to remove as much more of the mother liquor as possible; after which the mass of crystals was dried at about 200°.

Very little of the sodium chloride was obtained from the solution by this method; so in this case the filtered saturated solution was boiled down to about half its volume, the crystals freed of mother liquor and dried.

Potassium dichromate solution reacts with organic impurities when heated; so a cold, saturated solution was made, filtered and subsequently boiled down until crystals began to appear on the bottom of the vessel. The solution was then cooled, etc., as before.

All of these salts decrepitate more or less violently when first heated, and some of the salt usually flies out of the crucible. This may be prevented by preheating in a closed crucible to a temperature 100° short of the melting point or until decrepitation ceases. This operation may of course be carried out once and for all on the whole stock of material.

The components of the two eutectics should be very intimately mixed, preferably by grinding them together in a mortar until quite fine. It is well also to preheat the ingredients before mixing.

Dicalcium borate was prepared from a particularly pure supply of calcium carbonate and either boric acid glass (B_2O_3) or recrystallized boric acid (H_3BO_3) which had been dried at a temperature below 100°.

TABLE III

Melting points of salts from different sources

Substance	Source	Melting points	Difference
Potassium dichromate	Purified	397.5°C	....
" "	Squibb	397.3	0.2°
" "	Baker and Adamson	397.1	0.4
" "	Merck	396.8	0.7
Potassium chloride	Purified	770.3	....
" "	Squibb	770.1	0.2
" "	Kahlbaum	770.1	0.2
Sodium chloride	Purified	800.4	....
" "	Squibb	800.4	0.0
" "	J. T. Baker	800.1	0.3
" "	Morton[17] (Purified)	799.9	0.5
Sodium sulphate	Purified	884.7	....
" "	Merck	884.6	0.1
" "	Squibb	884.4	0.3
Potassium sulphate	Purified	1069.1	....
" "	Merck	1069.0	0.1
" "	Squibb	1068.9	0.2
" "	J. T. Baker "Special"[18]	1067.9	1.2

[17] This was table salt, "Morton's Free Running Salt—It Pours." It was further purified by dissolving, filtering the solution and recrystallizing it.

[18] This bottle had been opened for some time and may possibly have become contaminated, though there was no evidence that such was the case.

The two ingredients were weighed out into a tared platinum crucible, heated slowly to about 1000° and held there for an hour to drive off the H_2O and CO_2. The crucible was cooled and weighed and enough boric acid added to bring the contents up to $2CaO \cdot B_2O_3$, stirring it into the partly sintered mass with great care in order to avoid loss of material. The process of heating and adding boric acid was repeated until the theoretical weight was attained. The latest obtainable value, 69.66 was used for the formula weight of B_2O_3. This is a slow process but, owing to the volatility of boric oxide, it seems the surest way to secure the pure compound. I have employed the same method successfully for preparing lithium metasilicate for use as a fixed point.

Table III is a list of the melting points of several samples of these salts as received from different sources, as compared with the melting points of carefully recrystallized samples of the same salts. All of the determinations for a given substance were made and the first determination of the group repeated before going on, in order to provide a check against any possible change in the thermocouple. The small differences, therefore, are independent of its calibration.

A Simplified Method for the Melting Points of Certain Metals

For the primary calibration of the thermocouples used in this work, a method was used which has been found particularly useful at the gold and palladium points. It may also be used with other metals or eutectics whose melting points are not affected by slight oxidation, provided a satisfactory melting point curve is obtained.

Except in the case of gold and palladium, which were furnished in the form of 0.6 mm wire, the metals were hammered out into a sheet about 1 mm thick. Dirt and iron were removed from the surface with a knife. A strip of this sheet 6 to 8 mm wide was bent double over the junction, the wires insulated from the strip with paper, and the metal squeezed down tightly on the couple. The paper, of course, chars, but the ash is found to provide sufficient insulation.

For the wire samples, a tight coil of 5 or 6 turns was made, just large enough inside to admit the two wires of the couple, which had been cut apart at the junction. These were thrust in from opposite sides and the coil flattened to hold them in place. It was not found necessary to insulate the wires, probably because melting began at the outside of the coil.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C.,
October 12, 1923.

VARIATIONS IN THE CATAPHORETIC MOBILITIES OF OIL DROPS IN WATER

By Melvin Mooney

Abstract

Cataphoretic mobilities of oil drops in water and weak electrolytes.—The cell used was a thin walled glass tube 20 cm in length and 6 mm in diam., with gold electrodes sealed into the ends, held in a vertical position. By means of a microscope, velocity measurements were made on suspended drops both along the axis and in the stationary layer $R/\sqrt{2}$ from the axis, where R is the inner radius. (1) *Variation with diameter of drop.* For emulsions of ten oils in distilled water, the mobility for a field of 10 volts/cm, was found to increase with the diameter D for the range from .0005 to .04 mm. This is also true for emulsions of Stanolind in weak electrolytes, but for .0008 normal $CuSO_4$ the mobility is constant. In all cases the drops were negatively charged. (2) *Variation with the potential gradient.* For the smaller drops the mobility is constant, but larger drops, above .02 mm, show a slight increase for fields of 10 volts/cm. (3) *Initial time lag.* Observation on a large drop in a capillary tube open at both ends and immersed in a dish filled with .0001 normal NaOH, indicates that the mobility increases with time during the first 5 or 10 sec. after the electric field is applied. (4) *Theory.* It is suggested that the electric double layer around a drop is considerably distorted by an external electric field, so that equilibrium is established rather slowly.

Endosmotic flow of water in a closed cylindrical tube.—(1) *Hydrodynamic theory* gives the velocity as a linear function of the square of the distance from the axis, with a zero value for $r=R/\sqrt{2}$. This was experimentally verified. (2) *Mobility past an oil surface* was measured after coating the inside surface of the cell with oil, and was found approximately equal to the cataphoretic mobility of large drops of oil in water. This is also true for .0004 molar $CuSO_4$ solution.

I. Introduction

ELECTRIC endosmose is illustrated in the motion of a liquid through a porous diaphragm which results when a potential difference is maintained between the two sides of the diaphragm. Helmholtz[1] was the first to develop a mathematical theory of the phenomenon, and the formulas which he obtained were found to agree with experimental results. According to Helmholtz's theory, as a result of contact potential there is a very thin double layer of equal and opposite charges of electricity at the boundary between the diaphragm and the liquid within its pores. It is assumed that the layer next to the diaphragm is fixed to the surface but that the layer within the liquid is free to move. Consequently when a potential difference is maintained between the liquid on the two

[1] Helmholtz, Wiedemann's Annalen der Physik, **7**, 333 (1879)

sides of the diaphragm, the mobile part of the electric double layer moves through the pores and carries with it, by viscous drag, the entire liquid content of the pores.

Cataphoresis is the motion, parallel to an external electric field, of a particle suspended in a liquid. This phenomenon, like endosmose, is explained on the assumption that there is an electric double layer at the boundary between the particles and the liquid. Both Lamb[2] and Smoluchowski,[3,4] working independently, have developed theoretical formulas for the cataphoretic velocity of a suspended particle. Lamb's theory is more general than Smoluchowski's in that it takes into account the possibility of a hydrodynamic slip at the surface of the particle; but there are no experimental results to indicate such a slip, and recent work on the orientation of surface molecules seems to indicate that such a slip would not occur. Consequently Smoluchowski's formulas will be used in comparing with theory the experimental results reported in this paper.

Smoluchowski's formula for the cataphoretic mobility of a particle is

$$m_c = u/X = K(\varphi_i - \varphi_a)/4\pi\eta, \tag{1}$$

where u = the velocity of the particle,
X = the external electric field in e.s.u.,
$\varphi_i - \varphi_a$ = the contact potential in e.s.u. between the interior of the liquid and the surface of the particle,
K = the dielectric constant of the liquid,
η = the coefficient of viscosity of the liquid.

Since the dimensions of the particle do not appear in the formula, the velocity of the particle should be independent of its size. This element of the theory has been verified by Burton,[5] working with Bredig solutions of silver, and by Hardy,[6] working with solutions of globulin. But observations have been reported which indicate, though with some uncertainty, that the mobility varies with the size of the particle. Also preliminary experiments with oil drops in water indicated a variation in velocity with the size of the oil drop. Hence the research herewith reported was undertaken for the purpose of studying this variation in velocity, using very dilute emulsions of oil in water.

[2] Lamb, Phil. Mag., (5) **25,** 52 (1888)

[3] Smoluchowski, Bull. Int. Acad. Sci. Cracovie, p. 182 (1903)

[4] Graetz, Handbuch der Elektrizitaet und des Magnetismus, Johann Ambrosius Barth, Leipzig, Vol. II, p. 381

[5] Burton, Physical Properties of Colloidal Solutions, Longmans, Green and Co., p. 144

[6] Hardy, Journal of Physiology, **29,** p. 26, (1903).

II. Apparatus

Attempts were first made to use a rectangular cell modelled after the one used by Ellis,[7] but larger. However, when used in a vertical position, convection currents in the water prevented any determination of cataphoretic velocities. The cell finally adopted is shown in Figure 1. It consists essentially of a straight glass tube *A*, about 6 mm in diameter and 20 cm long, with gold electrodes *E* cemented into the ends of the tube. One of the electrodes has a small hole through its center to allow for expansion of the water in the cell while sealing the electrode in place.

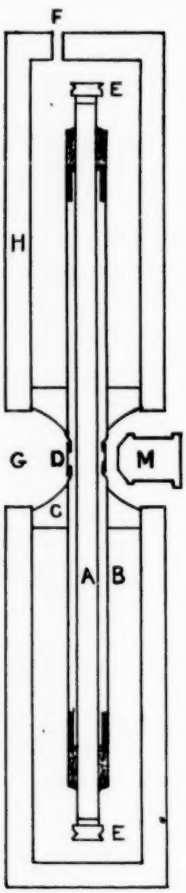

Fig. 1

In order to maintain uniform temperature the glass tube is surrounded by the brass tube *B*, cemented to the glass tube at either end. In the middle of this tube are two openings *D* for the purpose of admitting light and of making observations with the microscope *M*, which are covered by miscroscope cover glasses, cemented to the brass. By using very thin glass tubing, about .2 mm in thickness, and by having water on the outside as well as on the inside of the glass tube, the distortion of the optical image of the drops, resulting from the curvature of the glass tube, is reduced to a minimum. Even so, there is still sufficient distortion to be annoying and to make the measurements of the diameters difficult. Another source of trouble lies in the ease with which the glass tube is broken. Some fifteen or twenty were broken and replaced during the course of the work.

To maintain constant temperature the cell is enclosed in a wooden box *H*, with openings *G*. In order to reduce the temperature effects of outside air currents, a small block of wood *C*, through which the cell passes, is cut to fit snugly into the box. This block and two electrodes and supports for the cell not shown in the figure, are all fastened to the door of the box, which is removable.

In most of the experimental work the cell was in the vertical position and the microscope horizontal. With this arrangement the motion of the

[7] Ellis, Zeitschrift für physikalische Chemie, **78**, p. 321 (1911)

drops under gravity is parallel to the stream lines due to the electric endosmose and the drops remain in a region where the water has a constant velocity; thus it is easier to control the drop and to make velocity measurements.

The counter electromotive force developed at the electrodes was measured by reducing the external voltage to that necessary to give zero current through the circuit. Temperature readings were made by means of a thermocouple, one junction of which was inserted into the wooden box, at F, while the other junction was kept in a mercury bath with a thermometer graduated at 1/5° C.

The microscope consisted of a 2/3-inch objective and a Ramsden eye-piece. Distances perpendicular to the axis of the microscope were measured by means of a glass scale in the eye-piece. The magnification of the objective with respect to this scale was 9.156 diameters. Distances parallel to the axis were measured by means of the graduated scale on the fine movement of the microscope. Time measurements were made with a stop-watch which gave readings to 1/10 sec. Ordinarily the distance on the eye-piece scale used for velocity measurements was chosen such that the time measurements was between 3 and 15 seconds. To absorb the heat rays from the light source a water cell 2 feet long was inserted.

III. Theory of the Closed Cylindrical Cell

Neglecting for the present the velocity of an oil drop due to gravity, the observed velocity due to the electric field is the resultant of the cataphoretic velocity and the velocity of the water in the neighborhood of the drop. Due to electric endosmose the water near the surface of the cell moves parallel to the axis; and since the cell is closed at each end, this motion results in a hydrostatic pressure gradient which causes the water along the axis to flow in the reverse direction. Lamb[8] has shown theoretically that in such a system the flow of the water follows the equation,

$$w = (P/4\eta)(r^2 - \tfrac{1}{2}R^2) \qquad (2)$$

where w = the velocity of the water; P = the hydrostatic pressure gradient parallel to the axis; η = the coefficient of viscosity of the water; r = the distance from the axis of the cell, and R = the radius of the cell.

From this the velocity at the surface is

$$w_R = PR^2/8\eta,$$

and Eq. (2) may be written,

$$w = w_R(2r^2/R^2 - 1). \qquad (3)$$

[8] Lamb, l. c.,[2] p. 58

Now for an oil drop which is small compared with the diameter of the cell we will assume that u, its velocity with respect to the water, is independent of its position in the cell. Then for v, the observed velocity of a given oil drop, we shall have,

$$v = u + w = u - w_R + (2r^2/R^2)w_R. \tag{4}$$

To test this equation experimentally the cell was placed on the microscope table in a horizontal position; and an oil drop of the right size to rise under gravity at a convenient rate was located near the bottom of the cell. Then as the drop slowly rose to the top of the cell it was driven back and forth by reversing the electric field, and its velocity measured. To obtain the displacement of the drop from the axis of the cell, its vertical height was determined from the scale on the fine movement of the microscope when the drop was in focus; and its lateral displacement was measured by the scale in the eye-piece. According to Eq. (4), the velocity of a drop is a linear function of the square of its distance from the axis of the cell.

In Fig. 2 the small dots and circles represent readings made when the drop was respectively below and above the axis. Due to slow convection currents in the water, successive points lie alternately too high and too low. To eliminate the effect of the convection currents, the large dots and circles are located midway between each adjacent pair of experimentally determined points; these are seen to lie approximately on a straight line.

On the basis of these results we can consider that Eqs. (3) and (4) are verified by experiment. It is evident from Eq. (3) that at a distance from the axis equal to $R/\sqrt{2}$ the water is stationary. The cataphoretic velocity can be determined therefore, merely by measuring the velocity of an oil drop in this stationary layer of water. However, the drops would generally be displaced more or less from this position, and the velocity gradient in this region of the cell is rather high. Therefore since the primary purpose of these experiments was to detect differences in mobility rather than to measure the absolute value of the mobility, most of the measurements were made near the axis of the cell, where the velocity gradient of the water was a minimum. For determining the absolute mobility a few measurements in each experiment were made near the stationary layer also.

For drops which were not exactly in the stationary layer or on the axis, the observed velocity required a correction. The required correction formulas can easily be obtained from Eq. (4).

The correction to be applied to v for drops near the axis comes out

$$+2(r^2/R^2)(v_0 - v_s), \tag{5}$$

and the correction for drops near the stationary layer is

$$+2\sqrt{2}\frac{(r-R\sqrt{2})}{R}(v_0-v_s)+2\frac{(r-R/\sqrt{2})^2}{R^2}(v_0-v_s) \qquad (6)$$

where v_0 and v_s are respecting the velocities of the drop on the axis and in the stationary layer.

The approximate value of (v_0-v_s) is obtained from the uncorrected observed velocities. As a rule the only term in either formula large enough to be of any importance is the first term in Eq. (6).

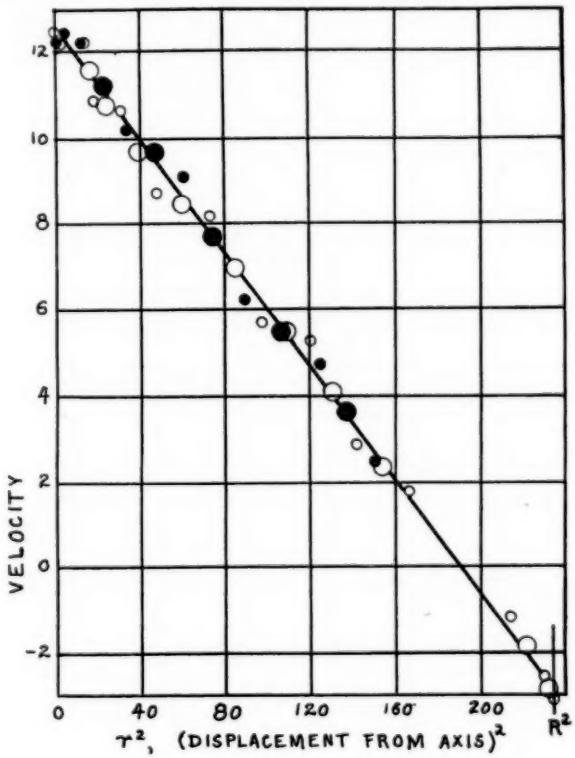

Fig. 2

IV. Experimental Determination of the Mobility-Diameter Curve

The experimental procedure was in general as follows. Two or three drops of the oil were shaken vigorously in a separatory funnel with about 200 cc of distilled water. The emulsion thus formed then stood for about a minute to allow the larger oil drops to settle out. One electrode was sealed in the cell, which had been cleaned with chromic acid and thoroughly washed with distilled water, and the cell was filled with the emul-

sion from the bottom of the separatory funnel. The other electrode was then sealed in place, the cell and the electrode cooled with tap water, and the small hole in the second electrode sealed up. It was then necessary to wait twenty or thirty minutes for the cell to come to uniform temperature. In order to prevent the oil drops from settling to one side, the cell was kept in a vertical position and frequently inverted during this interval. After a sufficient lapse of time velocity measurements were made on a series of oil drops near the axis of the cell; and next on a series near the stationary layer. Of course, there was constant movement of the drops under gravity; and even when there was no electric field, there were slow currents in the water. It was found, however, that within experimental error the resultant vertical velocity of a drop without the electric field was equal to half the difference between the upward and downward velocities with the electric field. Consequently the velocity due to cataphoresis and endosmose, free from the effects of gravity and of convection currents, is obtained by taking the arithmetic mean between the upward and downward velocities under the electric field. Each velocity was calculated from the average time obtained from two or three measurements. The diameter was measured on the scale in the eye-piece, the drop being held as nearly stationary as possible by applying just sufficient voltage to counterbalance the velocity of the drop under gravity.

A typical graph obtained in this way is shown in Figure 3, in which the velocities corrected according to Eqs. (5) and (6) are plotted against D, the diameter of the drop. Throughout this paper, diameters and velocities will be given in scale divisions, each equal to .001092 cm. The horizontal line gives the velocity of the water on the axis and is obtained from the difference between the upper and lower curves. Except for sign, the line also gives w_R, the velocity of the water at the surface of the tube.

The applied voltage was 199, giving 197.5 as the effective voltage E, after subtracting 1.5 volts for the counter electro-motive force.

The points enclosed in the dotted circle in Fig. 3 were the first three points obtained; and it was often observed that the first few points obtained in a series of measurements were low. The reason for this has not yet been thoroughly investigated; but it seems likely that this effect is due to a change in the conductivity of the water near the electrodes. It is difficult to keep the electrodes clean while sealing them in place; and a very small amount of impurities diffusing away from the electrodes into the pure water would increase the conductivity near the electrodes and hence increase the potential gradient in the middle of the cell.

These results prove that for oil drops of the size investigated ranging in

diameter from $.05 \times 10^{-3}$ to 4×10^{-3} cm and for a field of 10 volts per cm the velocity in pure water is not even approximately constant. It was found difficult, if not impossible, to work with drops outside of this range since larger drops move too fast under gravity and smaller drops are difficult to see and to measure accurately with the magnification used. But the results obtained seem to indicate that as the diameter increases the mobility approaches asymtotically an upper limit. Whether the

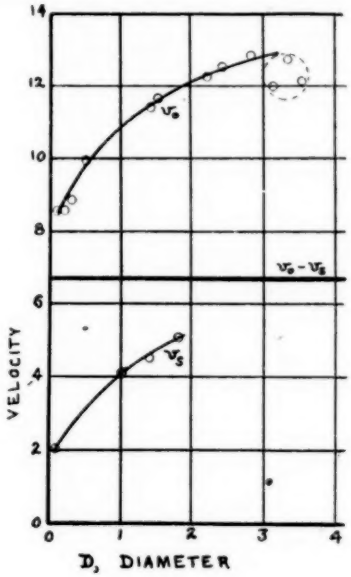

Fig. 3

lower limit, as D approaches zero, is zero or finite, is hard to judge from the curves so far obtained.

The oil used in the measurements shown in Fig. 3 was "Nujol," a commercial oil consisting of saturated hydrocarbons of the paraffin series. Quite similar results were obtained with a number of other oils, namely:

Bromoform, $CHBr_3$;

Bromonaphthalene, $C_{10}H_7Br$;

Dimethyl anilin, $C_6H_5N(CH_3)_2$—see Fig. 4, c;

Iodo-benzene, C_6H_5I—see Fig. 4, a;

Phenetol, $C_6H_6OC_2H_5$;

Phenyl mustard oil, C_6H_5NCS;

Tri-brom-hydrine, $CH_2Br \cdot CHBr \cdot CH_2Br$—see Fig. 4, b;

m-Xylene, $C_6H_4(CH_3)_2$;

"Stanolind," a paraffin hydrocarbon much like Nujol.

In all cases the motion was in the direction of the external field, indicating a negative charge on the surface of the drop. In Fig. 4 are shown

the mobility-diameter curves for iodo-benzene (a), tri-brom-hydrine (b) and dimethyl anilin (c). The curves (a) and (c) are extreme types, the curves for all the other oils lying between these limits.

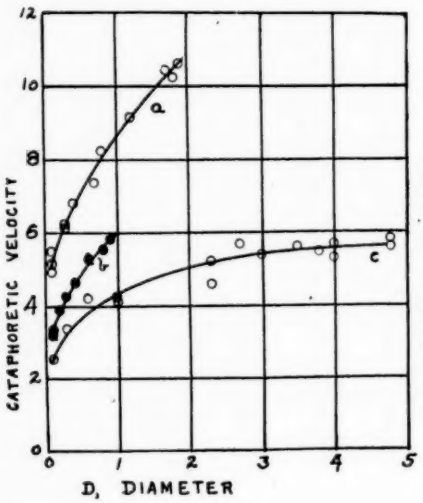

Fig. 4

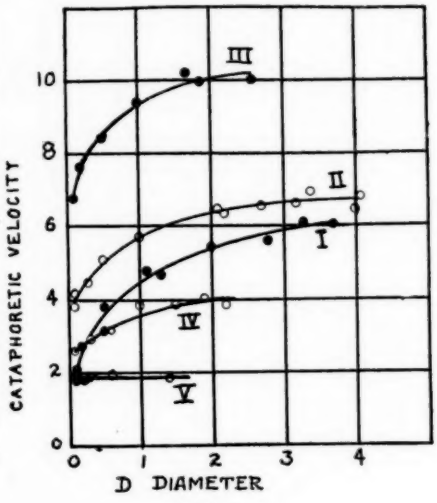

Fig. 5

Curve	Electrolyte	Normality
I	Impurities?	.00002
II	NaOH	.0001
III	NaOH	.001
IV	HCl	.0001
V	$CuSO_4$	.0008

Further experiments were carried out to determine the effects of added electrolytes and of variations in the potential gradient. Some of the results here reported are obviously only preliminary and require further extension and refinement before they can be accepted as final.

V. Effects of Electrolytes on Mobility

The cell used in these experiments was not designed for use with electrolytes, and with only moderate concentrations the electric current is so great that bubble formation at the electrodes makes measurements impossible. However, enough data were obtained with dilute solutions of a few electrolytes to indicate the general effect of added electrolytes on the nature of the mobility diameter curve. "Stanolind" is well suited for this purpose because of its chemical inertness. In Fig. 5 are shown the results obtained with Stanolind with various concentrations of sodium hydroxide, hydrochloric acid and copper sulphate. The concentrations of the electrolytes are given under the figure. The concentration of

impurities in the distilled water (Curve I) was estimated from the specific conductivity of the emulsion.

Curve V shows that with an .0008 normal solution of the divalent electrolyte $CuSO_4$ the mobility curve becomes practically a horizontal straight line. The effect of the monovalent electrolytes, though not so marked is similar, as can be seen from a comparison of the different curves.

VI. Effect of Potential Gradient on Mobility

According to Eq. (1) cataphoretic mobility should be independent of the external field. Moreover, according to Smoluchowski's theory the endosmotic mobility[9] is also independent of the potential gradient. This theory was tested rather carefully for pure water and was found to hold within experimental error for endosmotic mobility and for cataphoretic mobility of the small drops; but for the large drops the mobility was found to increase with the potential gradient.

Table I

Values of v/E

	(I)	(II)	(III)	(IV)	(V)
r:	$R/\sqrt{2}$	0	0	0	0
D:	.1	.1	.2	2.0	2.1
20 volts	....	....	53.5	96.2	97.6
			51.7		
50 volts	68.5	49.3	50.4	94.0	100.5
	62.2	50.0	51.5		
	69.1				
100 volts	....	....	51.8	99.1	101.4
			52.1		
200 volts	65.5	49.6	52.3	100.2	107.0
	65.4	49.6	52.4		
	65.4				

In Table I are given some of the results obtained in the experiment. The figures represent in arbitrary units the values of v/E, where v is the mean of several corrected velocities and E is the effective voltage; that is, the applied potential after being corrected for the counter e.m.f. The results in Column I, obtained with a small drop near the stationary layer, show that the cataphoretic mobility of small drops is independent of the potential gradient within experimental error for the range 50 to 200 volts. This being established, the results in Column II, obtained

[9] Endosmotic mobility is here used to mean the velocity per volt per cm. of a liquid moving past a fixed surface under the influence of an electric field parallel to the surface. It is understood, of course, that the liquid considered is sufficiently far from the surface not to include any of the electric double layer.

with a small drop on the axis, show that the endosmotic mobility also is independent of the voltage over the same range. It is difficult to obtain consistent results in the stationary layer with voltages much less than 50; but measurements on the axis with voltages from 20 to 200 gave the results in Column III. This shows that the sum of cataphoretic and endosmotic mobilities is constant in this range of voltage; and it seems most probable, therefore, that each mobility is constant. Columns IV and V show the results obtained with larger drops on the axis. If we subtract from the observed velocity the component due to the motion of the water along the axis, we find that the difference in cataphoretic mobility for the large drops at 200 volts and at 50 volts is about 15 percent of the mobility at 200.

Attempts to extend these measurements with small drops to voltages lower than 20 led to inconsistent results, which seemed furthermore improbable, for they indicated a large increase in mobility at low voltages. Attempts were made to obtain the effective voltage within the cell from Ohm's Law by making simultaneous measurements of the current through the cell at different voltages while velocity measurements were being made; but the results were still inconsistent. It was therefore decided to try a different cell, much longer and of smaller diameter, thereby reducing both the convection currents in the water and the relative importance of the counter e.m.f. A glass tube was drawn out into a thin-walled capillary about 120 cm long and 1 mm in diameter. It was then bent so as to fit into a shallow glass dish, 10×23 cm, which could be held on the microscope stage. The cell was filled with an emulsion of Stanolind in .0001 normal NaOH, electrodes were sealed into the ends, and the cell was immersed in water in the glass dish. For this work a higher powered objective was used in the microscope, giving a magnification of 45 diameters with respect to the scale in the eye-piece. Measurements were attempted only along the axis of the cell. The results are tabulated in Table II, the data being arranged in columns in the

TABLE II

	$D=.2$			$r=0$			
Volts:	200	50	200	20	200	50	200
v/E:	19.2	20.9	23.1	24.7	24.2	22.2	24.7
	19.7	24.1	24.7	26.5		22.2	24.6

order in which the measurements were made. The potential gradient in this case is about 1/5 of what it is for corresponding voltages in Table I. The limit of error at such low potential gradients is rather high, but within that limit the mobilities are constant.

In concluding this report of the experiments on mobilities, one very interesting observation will be described in detail, for it seems to give some new information as to the mechanism of the phenomenon of cataphoresis. The glass dish used in the last described experiment was filled with .0001 normal NaOH; and a straight capillary tube, open at both ends and about 19 cm long, was filled with an emulsion of Stanolind in .0001 normal NaOH and immersed in the water in the dish in a horizontal position. Electrodes of platinum wire dipped into the water near the ends of the tube. With this arrangement the water in the tube moves through it under the influence of endosmose without any reverse flow along the axis; and the velocity gradient in the tube is practically zero. The observations were made on a rather large drop ($D=1.6$) at the upper surface of the tube. It should be mentioned, however, that many results previously obtained indicate that the proximity of the surface of the tube would have little effect on the velocity of the drop. For example, in the experiments of the kind first described, in which the velocity of the drop is measured in different parts of the cell, there is no large deviation from the straight line shown in Fig. 2 when the drop reaches the surface.

The peculiarity in the behavior of this drop was that, with an applied potential of 200 volts, the drop gradually changed the direction of its motion a few seconds after the switch was thrown on. Since the velocity of the drop with respect to the water is in the opposite direction to the velocity of the water itself, this means that shortly after the current is applied, either the velocity of the water decreases or the velocity of the drop with respect to the water increases. Results already reported indicate that it would be the velocity of the drop that changes; and this is also indicated by the fact that the smaller drops in the capillary seemed to have constant velocities.

It was furthermore noticed that the behavior of the drop depended on its previous treatment. If the electric field was left on for some time and then suddenly reversed, the drop traveled the maximum distance, about .008 mm, and the maximum time, about 6 seconds, before reversing the direction of its motion. If the electric field, instead of being reversed, was merely interrupted for about a fifth of a second, the motion of the drop continued immediately in the same direction without reversal. The effect of previous treatment on the behavior of the drop was still noticeable if 5 or 10 seconds were allowed to intervene from the time the switch was taken off to the time the field was reversed; but the longer the time interval which intervened, the less the time and the shorter the distance the drop traveled before reversing its direction of motion.

The only interpretation of these observations which occurs to the author is that the effect of the external field is to displace with respect to the drop the positive ions constituting the mobile part of the electric double layer; that the final distribution of the charge in the neighborhood of the drop is established only after an interval of several seconds, being opposed by the negative charge on the surface of the drop and by the conductivity of the water near the drop; but that the drop moves faster with this final distribution than it does with the symmetrical distribution that obtains when there is no external field. If this explanation is correct, it seems furthermore probable that the distortion of the charge distribution is considerable. Some of the positive charge may even be drawn completely away, leaving the drop and the surrounding water with a net negative charge.

This theory would readily explain the increase in mobility of the large drops with potential gradient, for the distortion of the charge distribution would no doubt increase with the potential gradient.

The question naturally arises whether the increase in mobility with diameter at 200 volts is due entirely to the increase in the mobility of the large drops with potential gradient; that is, whether the limiting value of the mobility of all drops would be the same as the voltage approaches zero. When it was found that the large drop in the horizontal capillary tube failed to stick to the surface, it was decided to measure its velocity at low voltages. The results obtained are shown in Fig. 6, where v/E is plotted against the applied voltage V. In this case, of course, the observed v is the difference between the final cataphoretic velocity of the drop and the endosmotic velocity of the water. The points represented by dots are the values of v/E at 200 volts for some small drops for which $D = .25$. The velocity of one of these small drops was measured at different voltages from 5 to 200, and it was found that for it v/E was constant and equal to about -6. It is evident, therefore, that the mobility of a large drop even at very low voltage is higher than the mobility of the small drops. If we take into account the velocity of the water through the tube and use previously measured values of endosmotic mobility for .0001 normal NaOH, we can calculate approximately the relative difference in cataphoretic mobilities at 5 volts between the large and the small drops and the relative difference in mobility for the large drops between 5 and 200 volts. We thus get 8 percent for the former and 20 percent for the latter.

For the small drops, also, by qualitative observations, it was possible to detect at 5 volts a variation in mobility with size of the drop. Two drops are chosen, say with diameters .05 and .2, which are very close

together. Drops as small as this rise very slowly under gravity, and with an applied potential of 5 volts, both drops will remain in the field long enough for a difference in their relative positions to be easily detected.

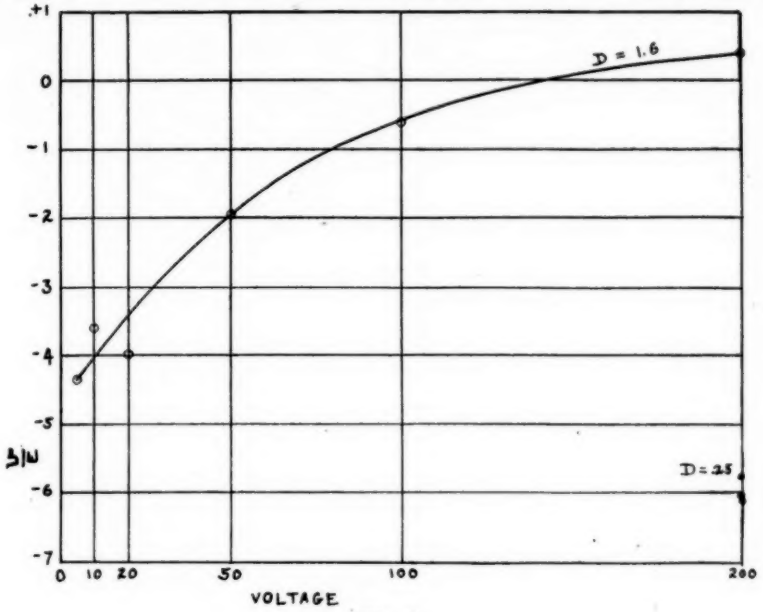

Fig. 6

A number of such comparisons were made and in all cases it was found that the mobility of the larger drop was the greater.

VII. Ratio of Cataphoretic to Endosmotic Mobility

Smoluchowski[3] has developed a theoretical formula for endosmotic mobility which, except for sign, is exactly similar to Eq. (1); so according to this theory the cataphoretic mobility of a sphere moving through a liquid is numerically equal to the endosmotic mobility of the same liquid moving past a surface of the same material as the sphere. So far as the author knows no experimental test of this relationship has ever been published.

If we had a cataphoretic cell whose walls were made of the same material as the particles suspended in the emulsion and if the cataphoretic and endosmotic mobilities were numerically equal, we would have, in our previous notation,

$$w_R = -v_s \tag{7}$$

hence

$$v_s = v_0 - v_s \tag{8}$$

$$v_0 = 2(v_0 - v_s). \tag{9}$$

These equations were tested by wetting the inside of the cataphoresis cell with oil before filling it with the emulsion. One experiment was performed with Stanolind in distilled water and another in .0004 molar $CuSO_4$. In the latter case the gold electrodes of the cell were replaced by copper electrodes. The results of the two experiments are shown in Fig. 7 and 8, respectively. The circles in the upper set of points indicate measurements made before those in the lower set and the dots indicate measurements made after those in the lower set. The reason for the difference in height between the dots and circles in Fig. 8 is most probably that the oil on the surface of the tube was spreading over the electrodes

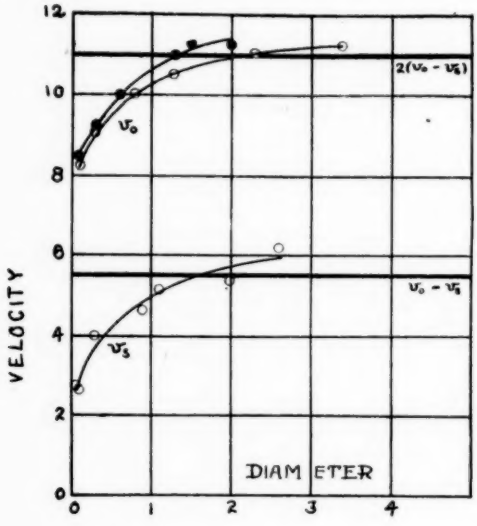

Fig. 7

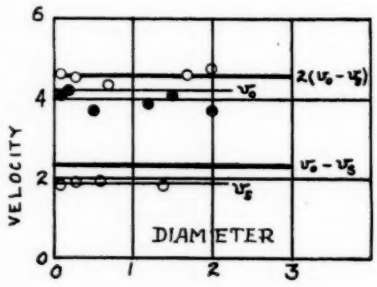

Fig. 8

and increasing the electrical resistance. This is indicated by the appearance of the electrodes after the experiment and by the fact that during the progress of the experiment the current through the cell fell off by several percent.

The results in Fig. 7 show that for the smaller drops in pure water the cataphoretic mobility at 10 volts per cm is less than the endosmotic mobility. In view of the variation with potential gradient in the mobility of the large drops, it appears that at low voltages their cataphoretic mobility would also not be greater than the endosmotic mobility and might even be less. The results in Fig. 8 show that in .0004 molar $CuSO_4$ the cataphoretic mobilities of both large and small drops are equal and approximately the same as endosmotic mobility. Here also there is some indication that the cataphoretic mobility may be a few percent less than

endosmotic mobility; but in view of the conditions of the experiment, that conclusion cannot be drawn with certainty.

This experimental work was begun under the direction of Dr. R. A. Millikan while he was still at the University of Chicago; and the author takes pleasure in acknowledging his great indebtedness to him for suggesting such a fruitful field of research.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
July 9, 1923.

THE SETTLING OF SMALL PARTICLES IN A FLUID

By Max Mason and Warren Weaver

Abstract

Settling of small particles in a fluid; mathematical theory.—Small particles immersed in a liquid experience a motion which is the combination of a steady gravitational drift and a Brownian movement. If there are space variations in the density of distribution of particles, the Brownian movement produces a diffusion which tends to equalize the density. In the steady state the density n of particles is an exponential function of x, the distance below the surface of the liquid. This paper investigates the *manner in which the steady state is established.* A consideration of the combined effect of fall and diffusion leads to a partial differential equation for the number density of particles as a function of depth and time. A set of special solutions is obtained in terms of which a solution satisfying initial and boundary conditions can be expressed. (1) *Liquid of finite depth.* The solution is obtained for a liquid of finite depth with an arbitrary initial distribution $n_0=f(x)$. For the case of uniform initial distribution a reduced form of the solution is obtained which contains a single parameter. This one parameter family of curves is plotted, and from these curves, either directly or by interpolation, may be obtained the density distribution at any time for a solution of any depth, density, and viscosity, and for particles of any size and density. For small values of t, since the solution obtained converges slowly, an image method is used to obtain an integral formula for the density. (2) *Liquid of semi-infinite or infinite depth.* In the case of a liquid of infinite depth the solution for an arbitrary initial distribution is expressed by the Fourier integral identity. The case of zero initial density for negative x, and constant initial density for positive x is calculated, as is also the case of particles initially uniformly distributed over a layer of depth h. In the case of a liquid extending from $x=0$ to $x=\infty$, the boundary conditions are satisfied by assuming a suitable fictitious initial distribution over the range from $x=-\infty$ to $x=0$. The cases of uniform initial distribution, and initial distribution over a layer, are calculated. The latter case, while derived for a liquid of semi-infinite depth, gives approximately the distribution of density during the settling of a layer of particles initially distributed uniformly over a depth h at the upper end of a very long column of liquid.

SMALL particles immersed in a liquid experience a motion which is the combination of a steady gravitational drift, the velocity of which is given by Stoke's law of fall, and a Brownian movement due to molecular bombardment. If there are variations of the density of distribution of particles, the Brownian movement produces a diffusion tending to equalize the density. If a liquid containing such particles stand undisturbed, a steady state is reached in which the density n of particles is an exponential function of x, the distance below the surface of the liquid, as has been verified experimentally by Perrin. It is the purpose of this

paper to investigate the manner in which the steady state is established. A consideration of the combined effect of fall and diffusion leads to a differential equation for the number-density of particles as a function of depth and time. The solution is obtained for an arbitrary initial distribution $n_0=f(x)$, both for a liquid of finite depth, and for a liquid of infinite depth.

1. The Differential Equation for the Non-Steady Case

The coefficient of diffusion can be obtained from a consideration of the steady state.[1] Suppose a gravitational force X to act on a spherical particle of radius a. Its velocity V is then given by Stoke's law of fall as

$$6\pi\mu a V = X,$$

where μ is the coefficient of viscosity of the liquid. Due to this velocity there will cross per second downward through unit horizontal area a number of particles given by

$$Vn = nX/6\mu\pi a.$$

The density distribution in the steady state is known to be given by

$$n = n' \, e^{(N/RT)X(x-x')}$$

where N is Avagrado's number, R the gas constant for a gram molecule, T the absolute temperature, and where n' is the density of particles at the position $x=x'$. It follows that the gradient of density in the steady state is given by

$$\partial n/\partial x = (N/RT)Xn.$$

The steady state, however, is characterized by the fact that the number drifting downward through unit horizontal area is equal to the number diffusing upward through the same area. The number of particles diffusing upward must therefore be given by

$$\frac{nX}{6\pi\mu a} = \frac{RT}{N6\pi\mu a}\frac{\partial n}{\partial x}.$$

Thus the factor by which the rate of change of density must be multiplied to give the flow of particles due to diffusion is $RT/N6\pi\mu a$. This quantity is therefore the desired coefficient of diffusion.

In the non-steady state there is, then, a net flow, per unit area, in the positive direction of x (that is, downward) given by

$$F(x,\, t) = \frac{n(x,\, t)X}{6\pi\mu a} - \frac{RT}{N6\pi\mu a}\frac{\partial n(x,t)}{\partial x},$$

where $n(x,\, t)$ is the number-density of particles at the place x and the time t. The net downward flow at the same time through a unit area a

[1] Einstein, Ann. der Phys. p. 554, 1916

distance dx lower is $F+(\partial F/\partial x)dx$; so that the net gain, per unit time, of the layer of thickness dx would be $-(\partial F/\partial x)dx$. That is

$$-\frac{\partial}{\partial x}\frac{1}{6\pi\mu a}\left[nX-\frac{RT}{N}\frac{\partial n}{\partial x}\right]=\frac{\partial n}{\partial t},$$

or

$$\frac{\partial n}{\partial t}=A\frac{\partial^2 n}{\partial x^2}-B\frac{\partial n}{\partial x}, \tag{1}$$

with

$$A=\frac{RT}{N6\pi\mu a};\ B=\frac{X}{6\pi\mu a}=\frac{\frac{4}{3}\pi a^3 g\delta}{6\pi\mu a}=\frac{2g\delta a^2}{9\mu}, \tag{2}$$

where δ is the effective density of the immersed particle; that is, its density minus the density of the liquid.

No particles cross the planes $x=0$ or $x=l$ where l is the depth of the liquid. Thus the net flow into the layer between $x=0$ and $x=dx$ is given by the net flow across the plane $x=dx$. Therefore

$$dx(\overline{\partial n}/\partial t)=(A\ \partial n/\partial x-Bn)_{dx},$$

where $\overline{\partial n}/\partial t$ is the average value of $\partial n/\partial t$ over the layer, and where the subscript dx on the parenthesis indicates that its value is to be given at $x=dx$. If dx is now allowed to approach zero, the equation

$$A\ \partial n/\partial x=Bn,\quad \text{for } x=0,$$

is obtained as one boundary condition. In the same manner it follows that

$$A\ \partial n/\partial x=Bn,\quad \text{for } x=l,$$

To these must be added the condition that the density reduce to the arbitrary distribution $n_0=f(x)$ for $t=0$. *The problem thus consists of finding a solution of the partial differential equation.* (1)

$$\frac{\partial n}{\partial t}=A\frac{\partial^2 n}{\partial x^2}-B\frac{\partial n}{\partial x},$$

under the boundary conditions

$$A\ \partial n/\partial x=Bn,\quad \text{for } x=0 \text{ and } l, \tag{3}$$

and the initial condition[2]

$$n_0=f(x),\quad \text{for } t=0. \tag{4}$$

The problem of the temperature distribution along a rod, insulated along its sides but radiating from its ends, differs analytically from the diffusion-fall problem here considered in the absence of the second term on the right side of (1). The differential equation (1) might be reduced to

[2] The differential equation here given was obtained by Th. De Coudres in an article, Ann. der Phys. 1894, which seems to be the only one previously published on the question. He did not attempt an exact solution under the boundary conditions, but limited himself from the beginning to approximate methods, studying in this manner the case of a liquid of finite depth.

the heat equation by the substitution $x'=x-Bt$. This substitution, however, would introduce a complexity in the boundary conditions, offsetting the gain in simplicity in the differential equation itself.

2. The Solution of the Differential Equation

If a solution of (1) be assumed in the form of a product of a function X of x alone by a function T of t alone, one obtains at once

$$T'/T=(AX''-BX')/X=\text{constant}=-r,$$

or the two ordinary equations

$$T'=-Tr; \quad AX''-BX'+rX=0,$$

where r is as yet unrestricted. A solution of the first of these equations is

$$T=e^{-rt}. \tag{5}$$

The solution of the second is

$$X=e^{Bx/2A}\ (C_1 \sin \omega x+C_2 \cos \omega x), \tag{6}$$

where

$$\omega=\sqrt{4rA-B^2}/2A.$$

Solving this last equation for r in terms of the new constant ω, substituting this in (5), and taking the product of (5) and (6) one obtains

$$n(x,t)=e^{-(4A^2\omega^2+B^2)t/4A}\ e^{(B/2A)x}\ (C_1 \sin \omega x+C_2 \cos \omega x). \tag{7}$$

3. The Boundary Conditions

The substitution of (6) in the boundary conditions leads to the equations

$$C_1\ \omega A-C_2\ \tfrac{1}{2}B=0,$$

$$C_1\ (\omega A \cos \omega l-\tfrac{1}{2}B \sin \omega l)-C_2\ (\tfrac{1}{2}B \cos \omega l+\omega A \sin \omega l)=0. \tag{8}$$

In order that these homogeneous equations possess solutions for C_1 and C_2, other than the trivial solution $C_1=C_2=0$, it is necessary that the determinant of the coefficients vanish. That is,

$$\sin \omega l\ (\omega^2A^2+B^2/4)=0,$$

so that

$$\omega=m\pi/l, \quad m=0, 1, 2, \ldots, \tag{9}$$

or

$$\omega=\pm i\ B/2A. \tag{10}$$

The constant ω having one of the values given by (9) or (10), the ratio of C_1 to C_2 is given by either equation (8). If one chooses

$$C_1=C_mB,$$

then

$$C_2=C_m\ 2m\pi A/l.$$

When ω has the value (10), r is zero so that T is unity, and the corresponding special solution of (1) is

$$C_0\ e^{Bx/A}.$$

It follows that the expression

$$n = e^{-(4A^2m^2\pi^2+B^2l^2)t/4A^2l^2}\, e^{Bx/2A} \sum_1^\infty C_m [B \sin (m\pi x/l) + (2m\pi A/l)\cos(m\pi x/l)] + C_0\, e^{Bx/A}, \quad (11)$$

satisfies (1) and the boundary conditions, C_m and C_0 being arbitrary.

It remains to satisfy the initial condition. For $t=0$ Eq. (11) gives

$$n_0\, e^{-Bx/2A} = f(x)\, e^{-Bx/2A} = C_0\, e^{Bx/2A} + \sum_1^\infty C_m [B \sin (m\pi x/l) + (2m\pi A/l)\cos(m\pi x/l)], \quad (12)$$

and it is necessary to determine the constants C_0 and C_m so that this equation will be satisfied. That is to say, it is necessary to expand an arbitrary function

$$\psi(x) = f(x)\, e^{-Bx/2A},$$

in a series of characteristic functions u_m, where

$$u_m = B \sin \omega_m x + 2A\omega_m \cos \omega_m x, \quad \omega_m = m\pi/l;\ m \neq 0$$
$$u_0 = e^{Bx/2A}, \qquad w_0^2 = -B^2/4A^2.$$

It is interesting to note that in order to obtain a complete set of characteristic functions, in terms of which an arbitrary function can be expanded, it is necessary to include the function u_0, which is so radically different in character from the other characteristic functions u_m.

The functions u_i satisfy the differential equation

$$u_i'' + \omega_i^2 u_i = 0 \qquad i = 0, 1, 2, \ldots, \quad (13)$$

and the boundary conditions

$$u_i' = B/2A\ u_i, \qquad x = 0 \text{ and } l.$$

Hence, integrating by parts,

$$\int_0^l (u_i''u_j - u_j''u_i)dx = [u_i'u_j - u_j'u_i]_0^l - \int_0^l (u_i'u_j' - u_j'u_i')dx = 0.$$

From equation (13) it follows however that

$$\int_0^l (u_i''u_j - u_j''u_i)dx = (\omega_j^2 - \omega_i^2)\int_0^l u_iu_j\, dx.$$

Hence the integral from 0 to l of the product u_iu_j of two characteristic functions vanishes when $i \neq j$. When $i = j$

$$\int_0^l u_i^2 dx = \tfrac{1}{2}(B^2 + 4A^2\omega_i^2), \quad i \neq 0.$$

Multiplying both sides of (12) by u_0 and integrating from 0 to l

$$C_0 \int_0^l e^{Bx/A}dx = \int_0^l f(x)dx,$$

and for the special case that the initial distribution is uniform, i.e. that $f(x) = \text{constant} = n_0$,

$$C_0 = Bn_0l/A(e^{Bl/A} - 1).$$

Multiplying both sides of (12) by u_m, where $m \neq 0$, and integrating from 0 to l,

$$\frac{4m^2\pi^2A^2+l^2B^2}{2l^2}\,C_m=\int_0^l e^{-Bx/2A}\,f(x)\left\{B\sin(m\pi x/l)+(2m\pi A/l)\cos(m\pi x/l\right\}dx.$$

For the case $f(x)=\text{constant}=n_0$ this equation gives

$$C_m=\frac{16A^2Bm\pi l^3}{[4A^2m^2\pi^2+B^2l^2]^2}\,(1\mp e^{-Bl/2A}),$$

with the upper sign holding for m even, the lower for m odd. The solution of (1) which satisfies the boundary and initial conditions is thus

$$n(x,t)=\frac{n_0\,Ble^{Bx/A}}{A(e^{Bl/A}-1)}+ \tag{14}$$

$$+n_0\,16\,A^2B\pi l^3e^{\frac{Bx}{2A}}\sum_1^\infty \frac{e^{\frac{(4A^2m^2\pi^2+B^2l^2)t}{4Al^2}}\,m(1\mp e^{-\frac{Bl}{2A}})\left[B\sin\frac{m\pi x}{l}+\frac{2m\pi A}{l}\cos\frac{m\pi x}{l}\right]}{[4A^2m^2\pi^2+B^2l^2]^2}$$

4. Reduction of the Solution

In (14) the density is expressed as a function of x and t, and of the three parameters A, B, and l. By making suitable substitutions in the differential equations and boundary conditions it is possible to obtain a reduced form of the solution, which contains a single parameter. This one parameter family of curves then furnishes the solution for any given A, B, and l. The Eqs. (1) and (3) through the substitutions

$$lx=y,\quad \frac{A}{Bl}=\alpha,\quad \frac{l}{B}=\beta,\quad \beta t'=t \tag{15}$$

are reduced to the form

$$\frac{\partial n}{\partial t'}=\alpha\,\frac{\partial^2 n}{\partial y^2}-\frac{\partial n}{\partial y},$$

$$\alpha\,\partial n/\partial y=n,\qquad y=0,\qquad y=1,$$

the solution of which, corresponding to (14), is

$$\frac{n}{n_0}=\frac{e^{y/\alpha}}{\alpha(e^{1/\alpha}-1)} \tag{14'}$$

$$+16\,\alpha^2\pi e^{(2y-t')/4\alpha}\sum_1^\infty \frac{e^{-\alpha m^2\pi^2t'}\,m(1\mp e^{-1/2\alpha})[\sin m\pi y+2\pi m\alpha\cos m\pi y]}{(1+4\pi^2m^2\alpha^2)^2}$$

In Figs. 1, 2, 3, 4, and 5 this equation is plotted for the values $\alpha=.025$, 0.1, 0.3, 0.5, and 2.0. For each value of α, curves are drawn for $t'=0.05$ 0.25, 0.50, 1.0, and ∞, except that such of these curves as practically coincide with the steady state curve $t'=\infty$ are omitted. The ratio, in the steady state, of the density at the bottom of the liquid to the density at the top is given by $e^{\frac{1}{\alpha}}$, the values of α plotted covering a range in this ratio from 1.65 to 2.35×10^{17}.

To illustrate the use of these curves a definite example will be considered. Perrin, in his observations of the variation with height of the concentrations of Brownian particles, experimented with gamboge grains of radius 0.212μ and density 1.194. These particles were immersed in

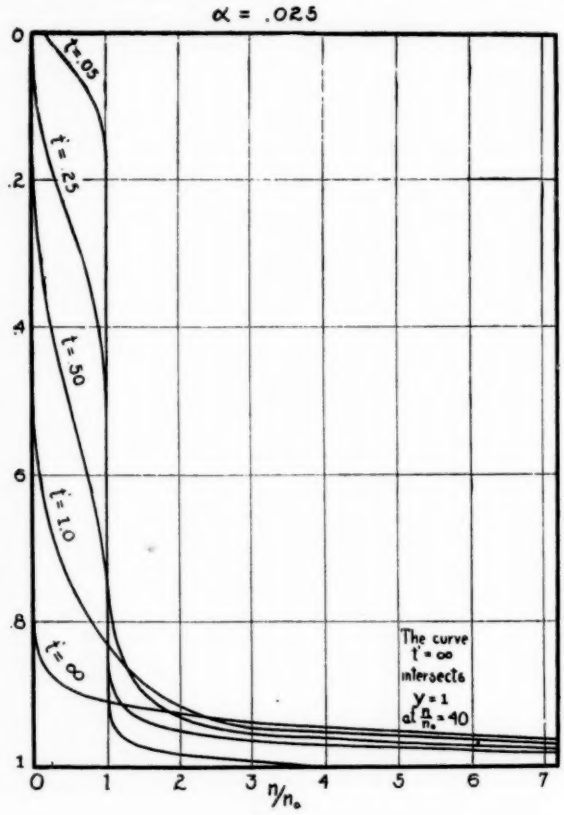

Fig. 1

water in a cell of depth 100μ. For these data it follows, from (2) and (15), that

$$A = 9.03\times10^{-9}, \quad B = 1.902\times10^{-6}, \quad l = 10,^{-2} \quad \beta = 5260, \quad \alpha = .475.$$

The curves for $\alpha = .475$ may be obtained by tracing on a single sheet the curves for $\alpha = .3$ and $\alpha = .5$ and interpolating. The result is shown in Fig. 6. In order to return to the original variables x and t it is necessary to multiply the ordinates by $l = 100\mu$, and the time t' by β. The curve $t' = 1$ or $t = 5260$ sec. sensibly coincides with the curve $t = \infty$ so that the steady state of distribution is practically established after about one and one half hours. Perrin remarks, "A few minutes suffice for the lower layers to become manifestly richer in granules than the upper layers. . . .

With the emulsions I have used, three hours are sufficient for the attainment of a well-defined limiting distribution in an emulsion left at rest, for practically the same values are found after three hours as after fifteen days." The information to be read from the curves is thus consistent with the observations of Perrin.

5. Liquid of Infinite Depth

In the case of a liquid which extends from $x=-\infty$ to $x=+\infty$ there are no boundary conditions, so that (7) is a solution for any value of ω.

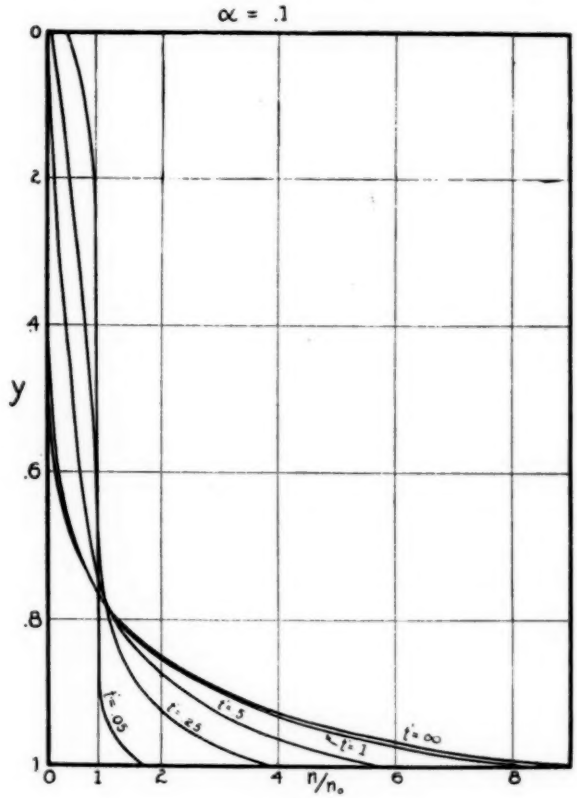

Fig. 2

The addition of all these solutions gives the solution

$$n=e^{-(4A^2\omega^2+B^2)t/4A}\ e^{Bx/2A}\int_0^\infty (C_1\sin\omega x+C_2\cos\omega x)d\omega,$$

where C_1 and C_2 are arbitrary. When $t=0$ this reduces to

$$e^{Bx/2A}\int_0^\infty (C_1\sin\omega x+C_2\cos\omega x)d\omega,$$

which, if the initial condition is to be satisfied, must be identical with the function $f(x)$. The comparion of this expression with the Fourier integral identity

$$\phi(x) = \int_0^{\infty} d\omega \int_{-\infty}^{+\infty} \phi(\gamma) \cos \omega(\gamma - x) d\gamma,$$

shows at once that the equation

$$f(x)e^{-Bx/2A} = \int_0^{\infty} (C_1 \sin \omega x + C_2 \cos \omega x) d\omega$$

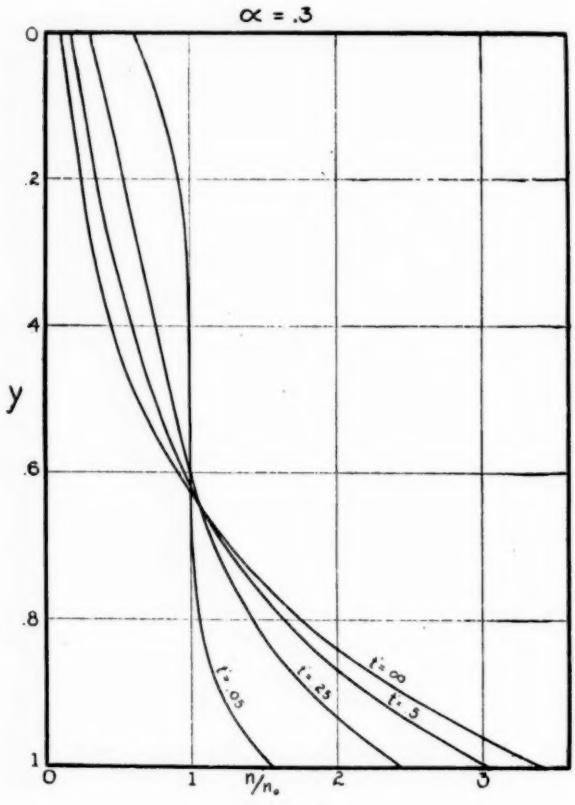

Fig. 3

is satisfied provided the constants C_1 and C_2 have the values

$$\pi C_1 = \int_{-\infty}^{+\infty} f(\gamma) e^{-B\gamma/2A} \sin \gamma\omega \, d\gamma,$$

$$\pi C_2 = \int_{-\infty}^{+\infty} f(\gamma) \, e^{-B\gamma/2A} \cos \gamma\omega \, d\gamma.$$

Thus

$$\pi n = \int_{-\infty}^{+\infty} f(\gamma) \, e^{-B\gamma/2A} d\gamma \int_0^{\infty} e^{-(4A^2\omega^2 + B^2)\cdot t/4A} \, e^{Bx/2A} \cos \omega(\gamma - x) d\omega,$$

satisfies the differential equation and the initial condition. If the integration with respect to ω be carried out this reduces to

$$n=(1/2\sqrt{A\pi t})\int_{-\infty}^{+\infty} f(\gamma)\ e^{-(\gamma-x+Bt)^2/4At}\,d\gamma. \tag{16}$$

If the initial density be zero for $x<0$, and a constant value n_0 for positive values of x, this expression takes the special form

$$n=(n_0/2\sqrt{A\pi t})\int_0^{\infty} e^{-(\gamma-x+Bt)^2/4At}\,d\gamma=\tfrac{1}{2}n_0\ [1-\Theta[Bt-x)/\sqrt{4At}], \tag{17}$$

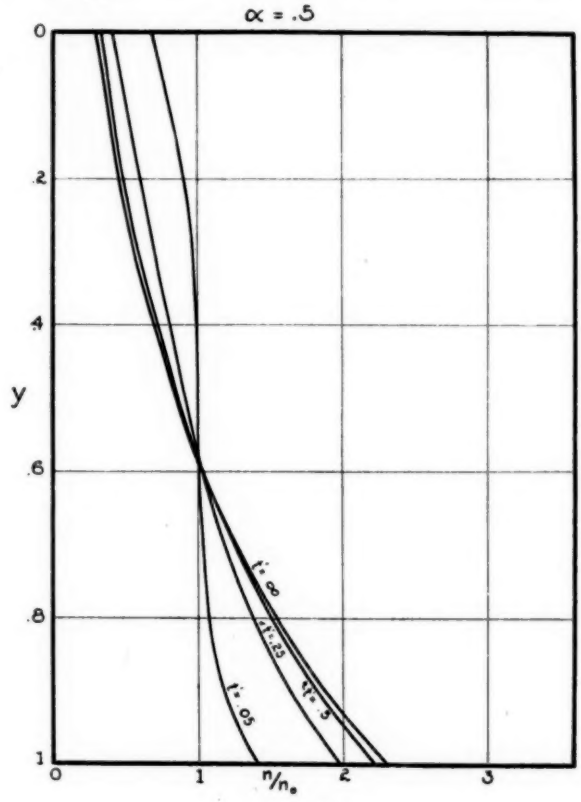

Fig. 4

where $\Theta(x)$ stands for the probability integral

$$(2/\sqrt{\pi})\int_0^x e^{-x^2}\,dx.$$

If the particles be initially uniformly distributed over a layer of depth h, so that

$$f(x)=0,\quad x<0 \text{ or } x>h;\quad f(x)=n_0,\quad 0<x<h,$$

equation (16) reduces to

$$n=\tfrac{1}{2}n_0\{\Theta[(h-x+Bt)/\sqrt{4At}]-\Theta[(Bt-x)/\sqrt{4At}]\}. \tag{18}$$

In terms of the running coordinate $x-Bt$, expressions (17) and (18) are of the same form as the expression for the one-dimensional diffusion of heat in an unlimited region, the initial distribution of temperature being, in the first case, constant for $x>0$, and in the second, constant over a layer of thickness h. Thus when the liquid extends indefinitely in both the positive and negative directions of x there is superimposed upon the steady fall whose velocity is B a diffusion entirely similar to the one-dimensional diffusion of heat. This statement also follows from the remarks at the end of §(1).

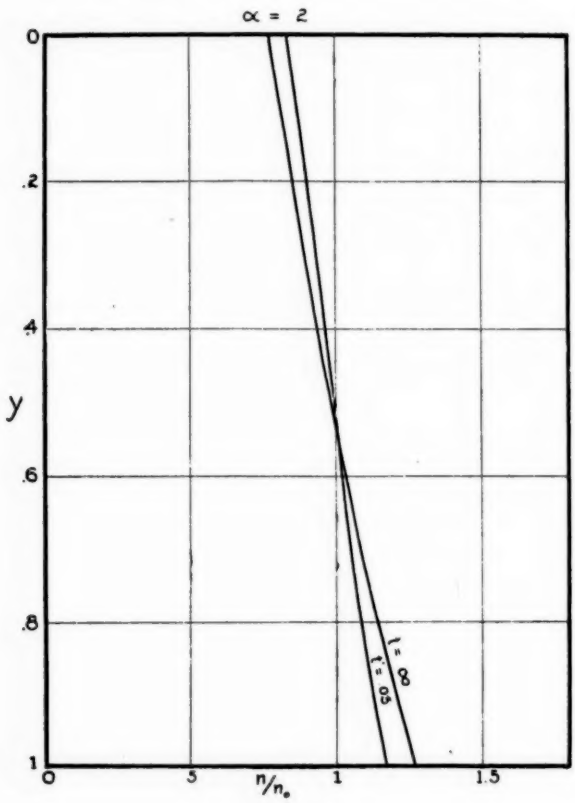

Fig. 5

If the liquid extends from $x=0$ to $x=\infty$ the initial distribution $f(\gamma)$ is given for positive γ only, and the boundary condition

$$A\ \partial n/\partial x = Bn, \text{ for } x=0, \tag{19}$$

must be satisfied. The problem can be reduced to the case just preceding by supposing that the liquid extend from $-\infty$ to $+\infty$, and that the region $x<0$ have an initial distribution of density of such nature that

the condition (19) will be satisfied for any t. If the boundary condition at $x=0$ is always satisfied it is obviously immaterial whether or not the liquid above $x=0$ actually exists. The solution (16) is thus available for this case provided $f(\gamma)$ for negative γ be determined in such a way that (16) satisfy (19).

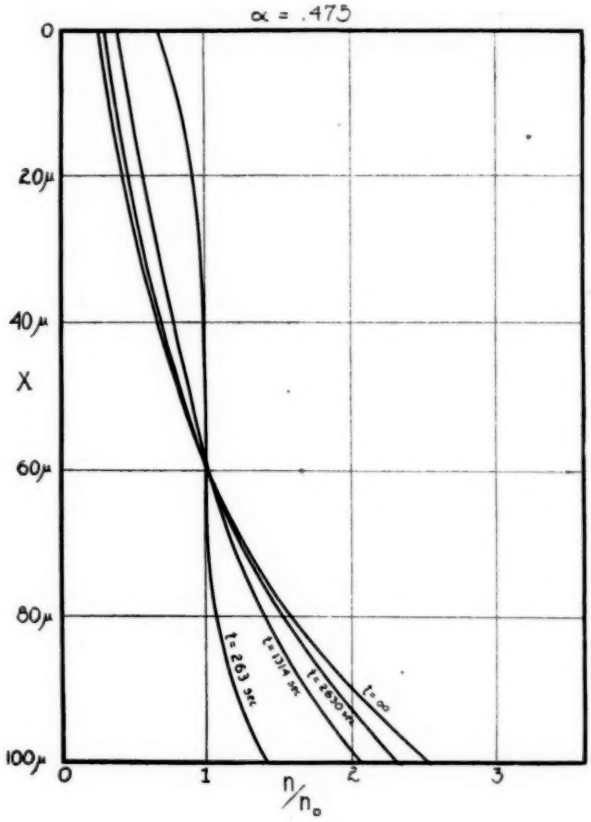

Fig. 6

If (16) be differentiated with respect to x and the result simplified by integration by parts the equation

$$\frac{\partial n}{\partial x}=\frac{1}{2\sqrt{A\pi t}}\int_{-\infty}^{+\infty}f'(\gamma)\ e^{-(\gamma-x+Bt)^2/4At}\,d\gamma,$$

results, it being assumed that $f(\gamma)$ is continuous at $\gamma=0$. Then to satisfy condition (19) the relation

$$\int_{-\infty}^{+\infty}[A\,f'(\gamma)-B\,f(\gamma)]\ e^{-(\gamma+Bt)^2/4At}\,d\gamma=0,$$

or

$$\int_{-\infty}^{+\infty}e^{-B\gamma/2A}\,[A\,f'(\gamma)-B\,f(\gamma)]\ e^{-\gamma^2/4At}\,d\gamma=0,$$

must hold identically in t. The factor $e^{-\gamma^2/4At}$ is even in γ, so that the condition will be satisfied if f be defined for negative values of γ so that

$$e^{-B\gamma/2A}\,[Af'(\gamma)-Bf(\gamma)] \tag{20}$$

is an odd function of γ. This condition gives a differential equation of the first order for $f(\gamma)$, $\gamma<0$, which, in combination with the assumed continuity of f at $\gamma=0$ uniquely determines f for negative γ in terms of the known f for positive γ. For example, if $f(\gamma)=\text{constant}=n_0$ for $\gamma>0$ then

$$f'(\gamma)-(B/A)\,f(\gamma)=(Bn_0/A)e^{B\gamma/A},$$

and

$$f(\gamma)=n_0\,e^{B\gamma/A}(1+B\gamma/A),\ \gamma<0,$$

so that the solution is

$$n/n_0=(1/2\sqrt{A\pi t})\left\{\int_{-\infty}^{0}(1+B\gamma/A)\,e^{B\gamma/A}\,e^{-(\gamma-x+Bt)^2/4At}\,d\gamma + \int_0^{\infty} e^{-(\gamma-x+Bt)^2/4At}\,d\gamma\right\} \tag{21}$$

which reduces to

$$\frac{n}{n_0}=-\frac{B\sqrt{t}}{\sqrt{A\pi}}\,e^{-(Bt-x)^2/4At}+\tfrac{1}{2}\left[1-\Theta\left(\frac{Bt-x}{\sqrt{4At}}\right)\right] + \tfrac{1}{2}\,e^{Bx/A}\left[1+\frac{B}{A}\,(Bt+x)\right]\left[1-\Theta\left(\frac{Bt+x}{\sqrt{4At}}\right)\right]. \tag{22}$$

As a second example suppose that the particles are initially distributed uniformly over a layer extending from $x=0$ to $x=h$; that is,

$$f(\gamma)=n_0,\qquad 0<\gamma<h. \tag{23}$$

Then, as before

$$f(\gamma)=n_0\,e^{B\gamma/A}(1+B\gamma/A),\quad -h<\gamma<0. \tag{24}$$

For values of γ less than $-h$, however, the equation

$$f'(\gamma)-(B/A)\,f(\gamma)=0,$$

gives

$$f(\gamma)=C\,e^{B\gamma/A}.$$

Evaluating the constant by means of the condition that $f(\gamma)$ is a continuous function, one has

$$C\,e^{-Bh/A}=n_0\,e^{-Bh/A}\,(1-Bh/A).$$

or

$$f(\gamma)=n_0\,e^{B\gamma/A}\,(1-Bh/A),\quad \gamma<-h. \tag{25}$$

If (23), (24), and (25) are substituted in (16) and the integrals evaluated the result is

$$\frac{n}{n_0}=\tfrac{1}{2}\,\Theta\left(\frac{h-x+Bt}{\sqrt{4At}}\right)-\tfrac{1}{2}\,e^{Bx/A}\left[1+\frac{B}{A}(x-Bt)\right]\Theta\left(\frac{Bt-x-h}{\sqrt{A\pi t}}\right) \tag{26}$$

$$-\frac{B}{A}\,e^{Bx/A}\sqrt{At/\pi}\,(1-e^{-(Bt-h-x)^2/4At})+\tfrac{1}{2}(1-Bh/A)\left[1+\Theta\left(\frac{Bt-x-h}{\sqrt{4At}}\right)\right].$$

This expression, while derived for a liquid of semi-infinite depth, approximately gives the distribution of density during the settling of a layer of particles, initially distributed uniformly over a depth h at the upper end of a very long column of liquid.

6. Integral Solution for the Finite Case

Eq. (14′) converges very slowly for small values of t, especially if a be small, so that it is unsuitable for calculation. An application of the image method sometimes used in heat problems furnishes an integral formula from which the density may be easily calculated when t is small.

If Eq. (16) be differentiated with respect to x, integrated by parts (assuming $f(\gamma)$ continuous), and substituted in the boundary conditions

$$A\ \partial n/\partial x = Bn, \qquad x = l,$$
$$A\ \partial n/\partial x = Bn, \qquad x = 0,$$

the result is the pair of equations

$$\int_{-\infty}^{+\infty} [f' - (B/A)f]\ e^{-(\gamma - l + Bl)^2/4At}\ d\gamma = 0,$$
$$\int_{-\infty}^{+\infty} [f' - (B/A)f]\ e^{-(\gamma + Bl)^2/4At}\ d\gamma = 0,$$

or

$$\int_{-\infty}^{+\infty} e^{-(B/A)(\gamma - l)} [f' - (B/A)f]\ e^{-(\gamma - l)^2/4At}\ d\gamma = 0,$$
$$\int_{-\infty}^{+\infty} e^{-B\gamma/2A}\ [f' - (B/A)f)]\ e^{-(\gamma^2/4At)}\ d\gamma = 0.$$

These two equations will be satisfied identically in t if the function

$$e^{-(B/2A)(\gamma - l)}\ [f' - (B/A)f] \tag{27}$$

is skew-symmetric about $\gamma = l$, and the function

$$e^{-B\gamma/2A}\ [f' - (B/A)f] \tag{28}$$

skew-symmetric about the origin $\gamma = 0$.

These two conditions suffice to determine $f(\gamma)$ for any γ provided the function is given over the range from 0 to l. Condition (27) "reflects" this given strip of the function, so that it is then given over the strip from 0 to $2l$: condition (28) then reflects this given strip about the origin, so that it is then given from $-2l$ to $2l$; and so on. If, for example, $f(\gamma) = n$ from 0 to l, the function from l to $2l$ is given by the equation

$$e^{-(B/2A)(\gamma - l)}\ [f'(\gamma) - (B/A)f(\gamma)] = (B/A)\, e^{-(B/2A)(l - \gamma)},$$

the solution of which is

$$f(\gamma) = (B\gamma/A)\ e^{(B/A)(\gamma - l)} + C\ e^{B\gamma/A}.$$

If the constant is evaluated from the condition that $f(\gamma)$ is continuous the result is

$$f(\gamma) = e^{(B/A)(\gamma - l)}\ \{1 + (B/A)\ (\gamma - l)\},\ l < \gamma < 2l.$$

In the same way the function in the range from $-l$ to 0 is determined from condition (28), reflecting about the origin. Thus

$$(\gamma) = ef^{(B/A)(\gamma+l)} \left\{1+(B/A)\ (\gamma+l)\right\},\ -l<\gamma<0.$$

If it were desired to establish a formula valid for any time it would be necessary to repeat this process indefinitely, but it is obvious that for t small the distribution in the range 0 to l will be affected only by the initial distribution in the immediate neighborhood. If the values here determined for the initial distribution in the range from $-l$ to $2l$ be substituted in (16) and the integration carried out the following formula results:

$$\frac{n}{n_0} = \tfrac{1}{2} e^{(y-1)/a}\left[1+\frac{y+t'-1}{a}\right]\left[\Theta\left(\frac{2-y-t'}{\sqrt{4at'}}\right)-\Theta\left(\frac{1-y-t'}{\sqrt{4at'}}\right)\right]$$
$$-\sqrt{\frac{t'}{a\pi}}\, e^{\frac{(y-1)}{a}}\left[e^{-\frac{(2-y-t')^2}{4at'}}-e^{-\frac{(1-y-t')^2}{4at'}}\right]+\tfrac{1}{2} e^{\frac{y}{a}}\left[1+\frac{y+t'}{a}\right]\left[\Theta\left(\frac{1+y+t'}{\sqrt{4at'}}\right)\right.$$
$$\left.-\Theta\left(\frac{y+t'}{\sqrt{4at'}}\right)\right]+\sqrt{\frac{t'}{a\pi}}\, e^{\frac{y}{a}}\left[e^{-\frac{(1+y+t')^2}{4at'}}-e^{-\frac{(t'+y)^2}{4at'}}\right]+\tfrac{1}{2}\left[\Theta\left(\frac{1-y+t'}{\sqrt{4at'}}\right)\right.$$
$$\left.-\Theta\left(\frac{t'-y}{\sqrt{4at'}}\right)\right], \qquad (29)$$

where y, t', and a are given by (15).

This formula was used in calculating the curves for $t'=0.05$ and $t'=0.25$ in Fig. 1. One of these curves was also calculated from (14) and the two checked.

UNIVERSITY OF WISCONSIN,
October 10, 1923.

THE PHYSICAL CRITERION FOR DETERMINING THE PITCH OF A MUSICAL TONE

By Harvey Fletcher

Abstract

Effects upon pitch and quality of musical sounds of eliminating certain component frequencies.—A high quality telephone system was used to reproduce musical sounds from the voice, the piano, the violin, the clarinet and the organ without any appreciable distortion. Into this telephone system electrical filters were introduced which made it possible to eliminate any desired frequency range. Results with this system show that only the quality and not the pitch of such musical sounds changes when a group of either the low or high frequency components is eliminated. Even when the fundamental and first seven overtones were eliminated from the vowel *ah* sung at an ordinary pitch for a baritone, the pitch remained the same. These results were checked by a study of synthesized musical tones produced by ten vacuum tube oscillators, with frequencies from 100 to 1000 at intervals of 100. It was found that three consecutive component frequencies were sufficient to give a clear musical tone of definite pitch corresponding to 100, and that in general when the adjacent components had a constant difference which was a common factor to all components, a single musical tone of pitch equal to this common difference was obtained, but not otherwise. *Explanation of the results in terms of mechanism of the ear.* Recent work on hearing has shown that the transmission mechanism between the air and the inner ear has a non-linear response which accounts for the so-called subjective tones. When the components of low frequency are eliminated from the externally impressed musical tone, they are again introduced as subjective tones before the sound reaches the nerve terminals. Calculation of the magnitude of these subjective tones from the non-linear constants of the ear shows that the results on pitch are what might be expected.

Sound spectra of ten typical musical sounds, obtained with an electrical automatic harmonic analyser to be described by Wegel and Moore, are given for *ah* sung at pitch *d*, *ā* sung at *a*, piano c_1, piano c', violin g', clarinet c, organ pipe c_1 for three pressures, and organ pipe c'.

THIS paper describes some experiments which show that the fundamental and a large number of harmonics from a compound tone may be eliminated without changing the pitch of the tone. This is contrary to the general belief that the pitch of a musical tone is determined by the vibration frequency of the fundamental. Although the idea of producing a musical tone which has a lower pitch than that corresponding to any single component frequency is not entirely new, the extent to which this method of producing low pitched tones can be carried has not been appreciated.

Composition of Musical Tones

A musical tone is usually composed of a large number of component frequencies. In the voice and in most musical instruments, it is well known that these components are harmonics, i.e. the component frequencies stand in the ratios of the integers 1, 2, 3, etc.; the characteristic quality of the tone is determined by their relative magnitudes.

Sound spectra for various types of musical sounds are shown in Fig. 1. In the charts shown in this figure the abscissas give the frequency in

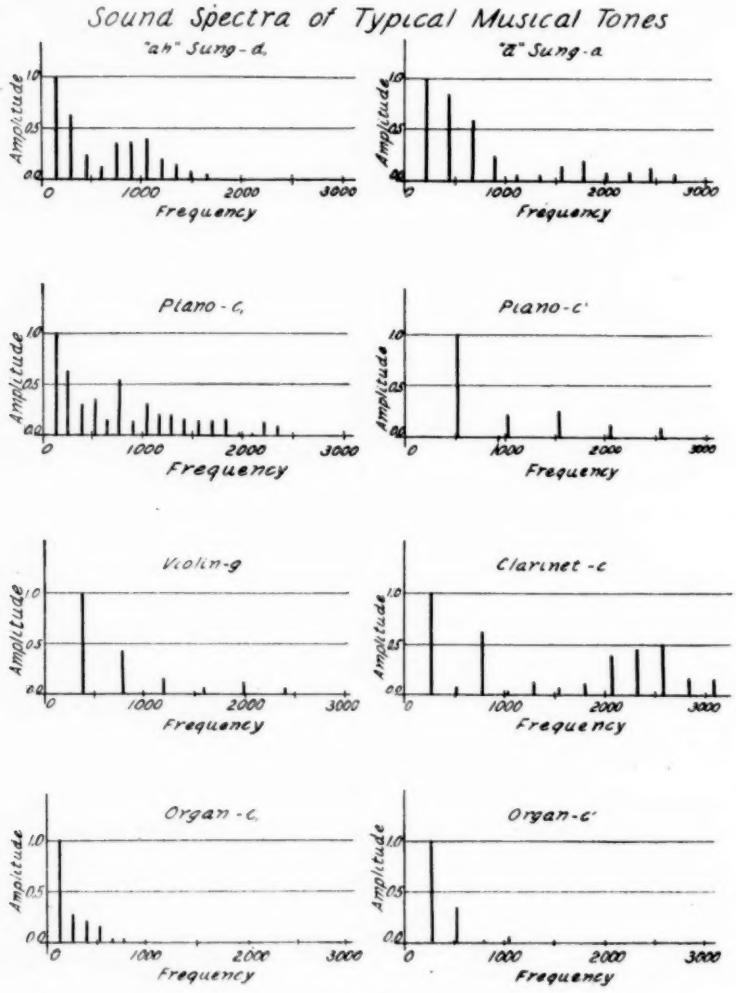

Fig. 1

double vibrations, or cycles per second. The ordinates give the relative amplitude of the harmonics, plotting the fundamental as unity. The

spectra for the piano represent the average values of the components during the first few seconds after the strings are struck. The sound spectra for organ pipes change very markedly when the blowing pressure changes. Those shown represent a typical case.

The analyses of these tones were made by the electrical harmonic analyzer which has been recently developed in the Bell System Research Laboratories. A full report covering the design and operation of this analyzer will soon be published by Wegel and Moore,[1] who are responsible for its development. The sounds to be analyzed are picked up by a condenser transmitter[2] which converts the sound wave into a faithful electrical copy. This electrical copy of the sound wave is then amplified and sent into the electrical harmonic analyzer for analysis. The analyzer consists essentially of a resonant circuit for which the frequency of resonance may be varied from 80 to 6,000 in steps of only a few cycles. Consecutive readings of the current transmitted through this circuit for each value of the resonant frequency are recorded photographically. The operations are entirely automatic, so that it requires only about five minutes from the time the machine is started until a completed picture of the sound spectrum comes out of the camera-box.

Measurement of the Pitch of a Musical Tone

The pitch of a tone as usually understood is the place on the musical scale to which the tone is referred. A pure tone,—that is, one consisting of a single component or frequency—has a definite pitch which anyone experienced in music will correlate with that frequency. By changing the frequency of such a pure tone its pitch can be made the same as that of any compound musical tone. Consequently a vibration frequency number can be associated with each pitch although, as will be seen presently, a component having such a frequency may not be present in the musical tone. The pitches as used in this paper are expressed on the International Tempered Scale, $a = 435$ cycles per second.

The pitch of the musical tones used in this investigation were determined by comparison with a standard, giving a fairly pure tone. This standard tone was produced by a telephone receiver, which was connected to a vacuum tube oscillator. Its pitch was adjusted to any desired value by making the proper setting on the oscillator.

The question might be asked, What happens to a tone if some of the upper harmonics are eliminated? Its is well known that the pitch is

[1] Wegel and Moore, presented before A.I.E.E. at Philadelphia, Feb. 8, 1924
[2] Wente, Phys. Rev. (2) **10**, 39, 1917

TABLE 1

Effect of the Elimination of Various Components on the Pitch and Quality of Various Musical Sounds

Source	Pitch	Eliminated components	Eliminated frequencies	Pitch change	Quality
Voice–*ah*	*d*(145)	F	0–250	No change	Inappreciable change
		F & 1–2	0–500	" "	Small change
		F & 1–4	0–750	" "	Large change
		F & 1–7	0–1250	" "	Very large change
		F & 1–9	0–1500	Uncertain	Noise
		6–∞	1000–∞	No change	Small change
		3–∞	500–∞	" "	Large change
		F& 1–2 & 6–∞	0–500 & 1000–∞	" "	Very large change
Voice–*ā*	*a*(218)	F	0–250	No change	Slight change
		F & 1–2	0–750	" "	Sounds like *ah*
		F & 1–4	0–1250	" "	Small change
		F & 1–5	0–1500	" "	Between *ah* & *ō*
		6–∞	1500–∞	" "	"
		3–∞	750–∞	" "	Sounds like *ō*
		F & 1–2 & 8–∞	0–750 & 2000–∞	" "	Very weak *ah*
Piano	*c*(129)	F	0–250	No change	Small change
		F & 1–2	0–500	" "	Metallic
		F & 1–5	0–750	" "	Clanging
		For more harmonics eliminated the tone lost all musical character			
		6–∞	750–∞	No change	No brilliance
Piano	*c*″(517)	F′	0–750	No change	Small change
		F & 1	0–1250	" "	Metallic
		All harmonics	750–∞	" "	Pure tone / Musical brill ance / lacking
Violin	*g*′(388)	F	0–500	No change	Large change
		F & 1	0–1000	" "	Very large change
		F & 1–2	0–1500	Uncertain	Non-musical
		2–∞	1000–∞	No change	Violin quality gone
Clarinet	*c*′(259)	F	0–500	No change	Large change
		F & 1–2	0–1000	" "	Very large change
		F & 1–4	0–1500	" "	Non-musical
		7–∞	2000–∞	" "	Large change
		2–∞	750–∞	" "	Pure tone (no clarinet quality)
Organ pipe	*c*(129)	F	0–250	No change	Small change
		F & 1–2	0–500	" "	Large change
		F & 1–4	0–750	Uncertain	Noise
		15–∞	2000–∞	No change	Very small change
		6–∞	750–∞	" "	Small change
Organ pipe	*c*′(259)	F	0–500	No change	Large change
		F & 1–2	0–1000	Uncertain	Non-musical
			2000–∞	No change	Small change
			750–∞	" "	Sounds dull

unaltered, but the quality of the tone is changed. An equally interesting question is, What happens to a tone if the fundamental and some of the lower harmonics are eliminated? The answer to this question is the

same as to the first one, namely, the pitch remains the same but the quality is altered.

Results

For the purpose of obtaining quantitative data relating to this question, use was made of the high-quality telephone system which has been described in previous papers.[3] The efficiency of this telephone system is approximately constant for the various frequencies throughout the range used in this investigation. Also, for the range of intensities which were used, the system has a linear response, so that no frequencies other than those in driving force were introduced. Consequently, the sound coming out of the receiver is a faithful copy of that which goes into the transmitter. Electrical filters[4] were introduced into this system, so that any portion of the spectrum could be eliminated. The characteristics of these filters were such that the amplitudes of the eliminated harmonics were reduced to values between .001 and .0001 of those obtained without the filter.

The results of the tests with the musical sounds indicated in Fig. 1 are shown in tabular form in Table 1. The judgments of pitch and quality were made by three persons familiar with music. In every case they agreed unanimously in the statements made in the 4th and 5th columns. The musical tones were produced at loudness[5] values between 70 and 80 units. These loudness values correspond approximately to intensities of 10^7 and 10^8 times the minimum audible intensity. In the second column of this table, the letter F refers to the fundamental and the numbers refer to the overtones, thus (F & 1–6) means that the fundamental and the first six overtones were eliminated. It is seen that the vowel *ah* sung at a pitch *d* is affected only slightly in pitch or quality when the fundamental and first two overtones are eliminated. Even with the fundamental and first six overtones eliminated, the pitch still very definitely corresponds to the pitch of a pure tone with the frequency of the fundamental, namely, 145 cycles per second. The harmonic analysis of this filtered tone shows no frequencies below 1000 cycles per second. Eliminating all of the overtones above the sixth changes the quality by about the same amount as eliminating the fundamental and first and second overtones. The data also indicate that if the fundamental and all of the upper and lower harmonics except the third, fourth and fifth

[3] R. L. Wegel, Journal A.I.E.E., October, 1921

[4] H. Fletcher, Jour. Franklin Inst. June 1922; also Phys. Rev. **15**, 513, 1920

[5] For the meaning of the term loudness as used here see article by H. Fletcher, Jour. Franklin Inst., Sept. 1923

are eliminated, the remaining compound tone has the same pitch as the fundamental, although the quality of the sound is very different from that of the sound *ah*.

As indicated in the table, similar results were obtained for the vowel *ā*, sung at the pitch *a*. Still other vowels were tried with similar results. In general, neither the quality nor the pitch of notes from a rich baritone or contralto voice is appreciably affected by eliminating the fundamental and the first two to three overtones. If, however, higher overtones are eliminated, the musical quality (in particular the richness) is noticeably affected and this is true even though the omitted overtones are all above the fifteenth. The high harmonics do not seem to be so essential for good quality in a soprano voice. Experimental tests showed the rather unexpected result that the elimination of all the harmonic frequencies above 2000 cycles affects the musical quality of a bass, a baritone or a contralto voice to a greater extent than the quality of a high soprano voice.

The table shows that the quality of the principal musical instruments is much more seriously affected by the elimination of the lower parts of their characteristic sound spectra than the quality of the sung vowels by a similar elimination. In any case such eliminations do not change the pitch, for this remains constant as long as the filtered sound can be recognized as a musical tone.

These results were confirmed in a very striking manner by using ten separate vacuum tube generators for producing the component frequencies. These generators were adjusted to give the frequencies 100 to 1000 at intervals of 100. They were all connected to a special telephone receiver and the currents regulated so that the pressure amplitude of the components of the sound emitted by the receiver were equal. By suitable switching arrangement any one of the components could be eliminated. When they were all impressed upon the receiver a full tone resulted which had a definite pitch corresponding to 100 cycles per second. The elimination of the 100-cycle component produced no noticeable effect. The elimination of any other single component had no effect upon the pitch and almost none upon the tone quality, although by careful listening, its introduction and withdrawal could be detected in most cases. Even with the first seven components eliminated, leaving only 800, 900 and 1,000, the pitch corresponded to a frequency of 100. When only two components were left, they were heard as separate tones, the fundamental subjective tone at 100 being still plainly audible but much weaker than either component. Any three consecutive components were sufficient to give the tone a pitch corresponding to 100, as, for example, 200, 300, 400 or 600,

700, 800 etc. When four consecutive components were sounded, the fundamental subjective tone was very prominent. When all of the components were sounded this fundamental seemed to be louder than the other components and dominated the tone.

The tests just described were made when the loudness[5] of the 700-cycle tone was at 90. When only three components, 700, 800, 900 were used and the loudness of the combination greatly decreased, it was found that the 100-cycle subjective tone disappeared when the loudness of the combination was approximately 45 units. At this loudness, the three tones were heard as separate tones, the 900 cycle one being the last to disappear as the loudness approached zero. When five or more consecutive components were used, the pitch seemed to remain the same for low values of the loudness even down to zero, although for these very low values, it was very difficult to judge pitch.

If the components 200, 400, 600, 800 and 1,000 were used, the pitch corresponded to 200 cycles, i.e. to the octave of the compound tone discussed above. This tone still had the same pitch when the 200 and 400 cycle components were eliminated. Any two consecutive pairs gave the subjective tone 200 but only very weakly. Combination 300, 600 and 900 gave a harmonious sound, the listener having the tendency to hear the combination as separate musical tones.

From the results which have been described, one might conclude that the pitch of a musical tone was determined by the common difference in the frequencies of the harmonics, rather than by the frequency of the lowest component. This conclusion suggested trying a combination of frequencies which are separated by a common difference, but which are not necessarily multiples of this common difference. The combination 100, 300, 500, 700 and 900 was tried and it was found to have no definite pitch, but sounded like a noise. However, one could distinctly hear the subjective tone at 200 cycles. Similarly, the combinations 100, 400, 700, 1,000 and 100, 500, 900 and 200, 500, 800 were tried and found to have no definite pitch and to be entirely lacking in musical quality.

Further evidence of the above phenomenon was made possible by means of a carrier telephone system which was available in the laboratory. The technique of carrier telephony makes it possible to displace all the frequencies constituting a compound tone by the same absolute amount upward or downward. Thus, if the compound tone of ten components which has been described were transmitted through such a system when the carrier at the transmitting end differed from the carrier at the receiving end by 30 cycles, the frequencies received would be 130, 230, etc. up to 1030. It is found that such a shift destroys the musical quality which

the original tone possessed. If the fundamental is very predominant this shift raises the pitch, but the inharmonic tones produce a harshness and the tone loses its musical character.

Structure of "Harmonic" Tones from Such Wind Instruments as the Bugle

In this connection it is interesting to examine the structure of those tones produced on wind instruments by changes in the blowing intensity rather than by changes in the length of the vibrating air column. When

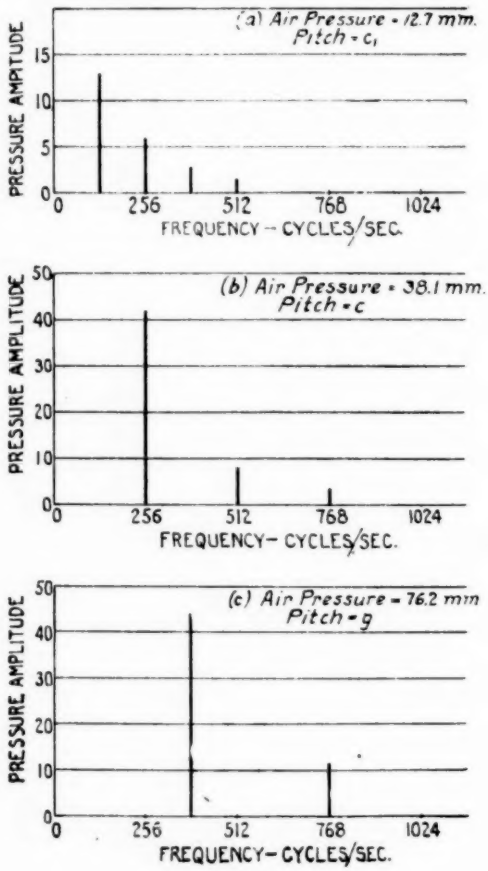

Fig. 2

the air pressure blowing an organ pipe or horn is continuously increased, the pitch of the emitted tone corresponds first to the fundamental and then it suddenly jumps to that corresponding to the first overtone and then to that corresponding to the second overtone, etc. As is well known, it is this effect that makes it possible to produce the different notes on

a bugle. One might expect to find all the harmonics of the fundamental in each of these notes. However, this would be contrary to the observations we have just described. In fact, we find from a few experiments upon organ pipes that the overtones are all present in appreciable amount when and only when the pitch of the tone is that corresponding to the fundamental but when the pitch corresponds to the first overtone, only those components which are multiples of the first overtone are perceptible. This is clearly shown in the sound spectra given in Fig. 2, obtained by means of the harmonic analyzer which has been described. They represent the sound emitted by an organ pipe when it was blown with the various pressures indicated on the charts.

Explanation of the Results

It is possible to explain these experimental facts concerning pitch from our conception of the mechanism of the ear. The recent work[6] on this subject which has been carried on in the Bell System Laboratories, has shown that the ear displays a non-linear response to external applied forces. This non-linearity produces subjective tones; all the summation, the difference, and the harmonic frequencies as well as the impressed frequencies produce nerve stimulation. When the fundamental and first few overtones are eliminated from the external tone, they are again introduced by the ear mechanism as subjective tones although of course with different intensities. The changes in the relative intensities of the components impressed upon the nerve endings produce the observed changes in quality.

For example, in Fig. 3, the top chart (a) shows that sound spectrum described above, which was produced by 10 oscillators working into a single telephone receiver. The currents from the oscillators were adjusted so that the pressure amplitudes produced in the outer ear canal were all equal to approximately 100 dynes per square centimeter. When these component tones are transmitted through the ear mechanism the relative amplitudes of the elements producing nerve stimulation are quite different from those shown in Chart (a). If the component tones are impressed separately upon the ear as single tones then the relative amplitudes of these elements which stimulate the inner ear would be represented by chart (b). The ordinates represent the relative sensitivity of the ear to the various frequencies.[7] If the ear had a linear response this same chart would represent the relative amplitudes when all the components were sounding simultaneously.

[6] See Wegel and Lane, Phys. Rev. **21**, 705, 1923; also Fletcher[4]

[7] See Fletcher and Wegel, Phys. Rev. **19**, 553, June 1922

The third chart (c) shows the redistribution brought about by the non-linearity of the ear, that is, it represents the actual spectrum produced in the average inner ear that is excited by the tone represented in chart

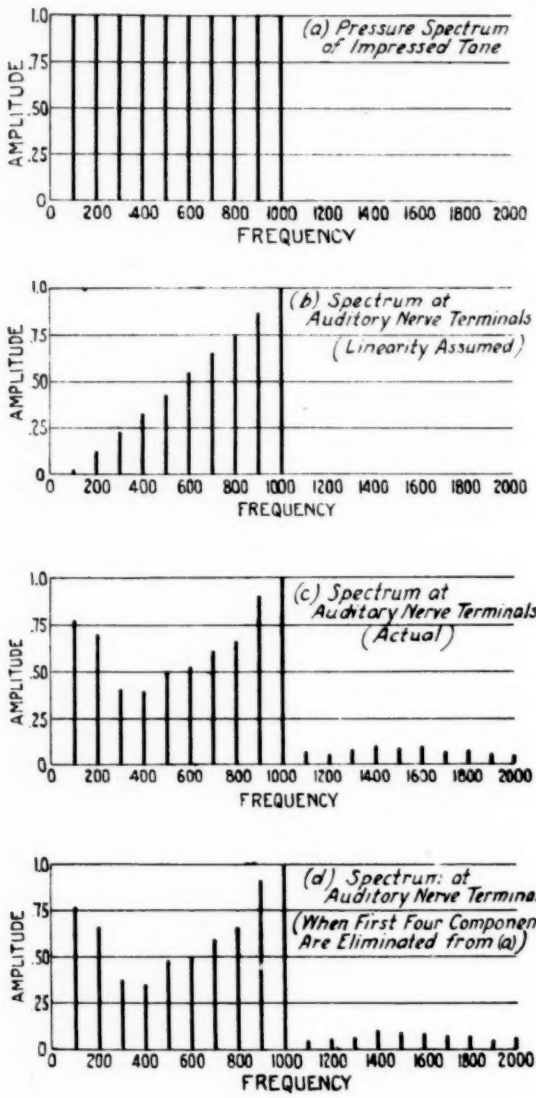
(a) Pressure Spectrum of Impressed Tone
(b) Spectrum at Auditory Nerve Terminals (Linearity Assumed)
(c) Spectrum at Auditory Nerve Terminals (Actual)
(d) Spectrum at Auditory Nerve Terminals (When First Four Components Are Eliminated from (a))
AMPLITUDE
FREQUENCY
1.0
.75
.50
.25
0
0 200 400 600 800 1000 1200 1400 1600 1800 2000

Fig. 3

(a). The fundamental is greatly increased due to the nine difference tones from adjacent components uniting to reinforce the fundamental.

The fourth chart (d) shows the spectrum in the inner ear when the first four components are eliminated from the impressed tone. That is, it

represents the condition when the oscillators which are sending out 100, 200, 300 and 400 vibrations per second are switched off. Since the lower components in the inner ear spectrum are principally due to the higher frequency components of the pressure spectrum, the elimination of the first few components of the latter spectrum produces very little effect upon the former.

The constants used in computing these redistributions were obtained from experimental measurements by Wegel and Lane[6] of the magnitudes of the subjective tones. A comparison of the last two charts shows very clearly why one should expect the pitch of the two tones to be the same. If the impressed tones are all decreased without changing their relative magnitudes the resulting inner ear spectra will be different from that shown in these charts. Consequently the quality of the musical tone as well as its intensity will change as the loudness of the musical tone approaches zero. For these low intensities the inner ear spectrum approaches that shown in chart (b).

RESEARCH LABORATORIES OF THE
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